ORGANIC CHEMISTRY

Synthetic Polymers and Dyes

Dr. R. K. Khandal
Director
ShriRam Institute for Industrial Research
19, University Road
Delhi – 110 007

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CONTENTS

Introduction
Classification of polymers
Polymerization
 Addition polymerization
 Condensation polymerization
 Phenol formaldehyde resins
 Urea formaldehyde resins
 Rearrangement polymerization
 Epoxy resins
 Polyurethanes
Rubber and Elastomers
 Natural rubber
 Synthetic rubber
 Eco-friendly polymers
Dyes
Classification of dyes

Introduction

The evolution and development of civilizations have always been associated with the development of newer materials simply because; the advancement of society has always created the need for improvements in the existing materials leading to the advent of new materials. As a result, the need for new and alternative materials ceases to exist.

If we study the history of materials, we would realize that the role, played by various materials, in the growth and evolution of human civilization is quite pivotal as well as essential. No surprises then, if the history of mankind has been described, based on various ages dedicated to the advent of various materials e.g. stone age, metal age etc.

If ancient history deals with materials used for hunting, agriculture and self -defense, the period up to the medieval age has seen the development of various alloys etc. Each time, with the exploitation of the existing resources to obtain different types of materials for various applications mainly for making life comfortable, the quest for new materials with more stringent criteria of performance improvements. Besides this, there has also been concern about the availability of naturally occurring non-renewable materials which have been depleting with time. Moreover, the quality of raw materials (mainly metal - based) has been on the decline because of the fact that the exploitation of minerals etc has been selective which means that what is available now if of much inferior quality.

During the last centuries, the efforts for the substitutes to the materials based on naturally occurring minerals have always been a priority for the scientists all over the world. As a result, a series of synthetic materials were developed for various applications. One of the most important class of materials is "polymer". It is only in the last hundred years that polymeric materials have become almost a household name in the world, replacing metals in many of the important applications.

The polymers actually gained overwhelming importance only during the early part of the 20^{th} century when it became evident that the polymers could replace almost all the conventionally used materials.

In fact, research in the field of material sciences during the last more than hundred years has mostly been dedicated either to demonstrate that the polymeric materials provide a better alternative to conventional materials or to develop the modified polymeric (composite) materials with properties not generally associated with the polymers used in making the composites. This way, research on polymers has been occupying the center stage and at times polymers have been considered as the real driving forces for most of the industrial applications as well as devices.

Today, we just cannot think of anything without having polymers been included in it. Thus, the present period of human civilization can easily be described as the "polymer age".

While it is true that polymer have not only changed our lifestyle but they have also made many of the devices possible (because of the unique structural attributes of polymers), it is a fact that this could happen only due to the concerted research efforts which included the studies dedicated to the understanding of the naturally available polymeric materials

The quest to develop new materials has always been due to the ever changing needs of mankind on the one hand and increasing knowledge base on all that exists around us on the other hand. For example, the development of polymers has also been possible only after it became known that polymeric structures existed in some of the natural materials. The human body functions, all of plant and animal tissues, and certain organic substances - such as proteins, chitin (hard coating of insects), cotton, silk, paper, rubber, wood, resin, etc. consists of polymeric (macromolecular) materials. Similarly, inorganic substances such as diamond, quartz, feldspar, concrete, porcelain, glass, are either entirely or substantially polymeric. It is only by the end of the 19^{th} century, it was clearly understood that all these substances possess only one essential common feature; they consist of very large sized (macro) molecules built with the combination of small basic units called monomers.

Thus, polymers are nothing but the union of large (repetitive) number of monomer molecules and they possess properties that are entirely different from their monomers. A polymer, therefore, is a substance consisting of molecules which are multiples of low molecular weight units; molecular weight being a measure of the weight of a molecule relative to a chosen standard. The low molecular weight unit making up the polymer is known as a monomer. The monomer units contain end groups that enable the monomers to join each other and form a large chain. If the number of monomer units in a polymer becomes very large, the latter is sometimes called a high polymer. In the case of some natural polymers, such as proteins, all the individual molecules have the same molecular weight and molecular structure. Further the monomer units can either be joined to each other in one direction or uni-dimensional or they may form a three-dimensional network. The polymers having the monomers joined uni-directionally are called straight chain polymers whereas the ones with the three-dimensional structure are also referred to cross-linked polymers.

With most of the synthetic and natural polymers, significant differences occur in the molecular weight of the individual macromolecules. Variability in the composition and molecular structures of polymers results from the type and nature of different end groups. The end groups determine: (a) the way in which the chain terminates, (b) variations in the arrangement of monomeric units and (c) irregularity in the sequence of monomeric units of different types if more than one type of monomer is present and irregularity in the sequence of monomeric units of different types if more than one type of monomer is present. The polymers with only one type of monomer are known as homopolymers and the ones with more than one monomer are termed as copolymers or heteropolymers.

In order to understand the fundamental aspects of polymers and polymeric materials, it is important that the following topics are described clearly,

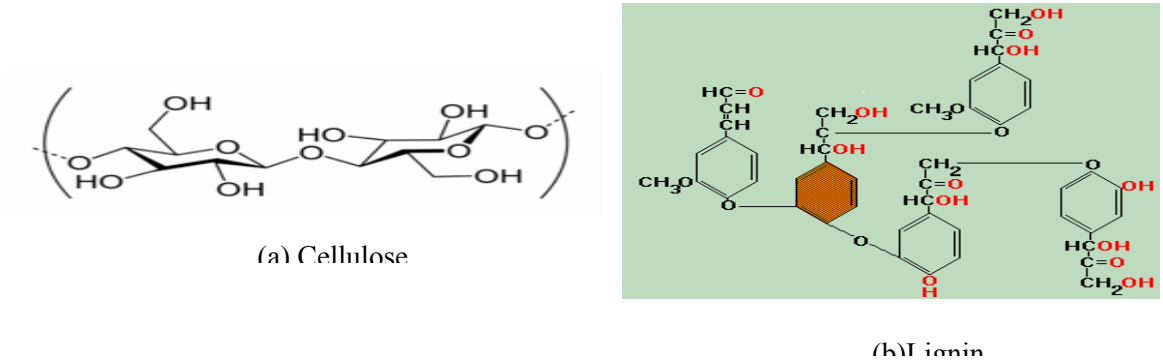
- Classification of polymers
- Types of polymers and their characteristics
- Methods of manufacture of polymers
- Polymeric materials and composites
- Industrial applications of polymers

The present chapter deals with all the above mentioned topics related to both the polymers and polymeric materials. The emphasis would be given more on the synthetic polymers, even though explanations would be provided for several characteristics of natural polymers.

Other than the polymers, this chapter also describes the synthetic dyes. Here, the emphasis has been on the basic fundamentals of dyes used for various applications etc.

Classification of Polymers

Polymers can easily be categorized into two major groups i.e. organic polymers and inorganic polymers. Further, each group can be divided into two classes known as natural polymers and synthetic polymers. The classification of polymers is further done based on the chemistry of the monomers, the process of polymerization, polymer structure and areas of their applications.

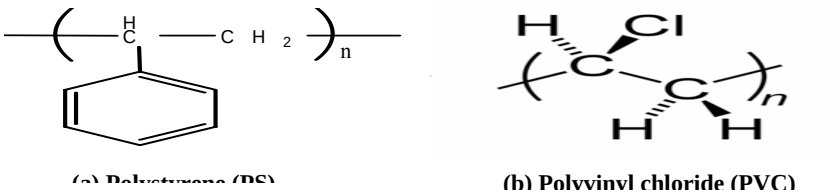


(a) Cellulose

(b)Lignin

Fig I: Examples of Natural Polymers

Lignin and cellulose, **Fig I,** are some examples of natural polymers and polyvinyl chloride and polystyrene, **Fig II,** are some examples of synthetic polymers.



(a) Polystyrene (PS) (b) Polyvinyl chloride (PVC)

Fig II**: Examples of Synthetic polymers**

Fig III gives a detailed classification of polymers. Natural polymers are those which are available to us by virtue of natural processes. In the case of organic polymers, all the natural polymers are produced by the living systems including humans, animals, microbes, plants, insects etc. The whole mechanism of polymerization in the living system is dependent on the genetic behavior of the living species. The genetic behavior is also determined by the polymeric structure of nucleic acids deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). As per the genetic behavior of the species, various organic polymers are produced mainly for the purpose of metabolic functions as well as for the functions required for furthering of the generations. For

example, various types of plants are capable of producing different kinds of carbohydrates like, starch, cellulose and amylopectins.

Proteins are also produced by several plant species and they are the preferred source of proteinaceous food for living beings, mainly humans. The plants also have the capacity to produce polymeric products such as terpenes, which find applications in a wide range of industrial sectors. The notable example is the product of natural rubber, which is nothing, but a polymer based on isoprene monomer. Chitin is another organic polymer, which find uses in various applications and such substances are produced by certain marine species. Lignin is another example of organic substance produced by plants. The detailed structure of each of the polymer has been shown in **Figs. IV – V.**

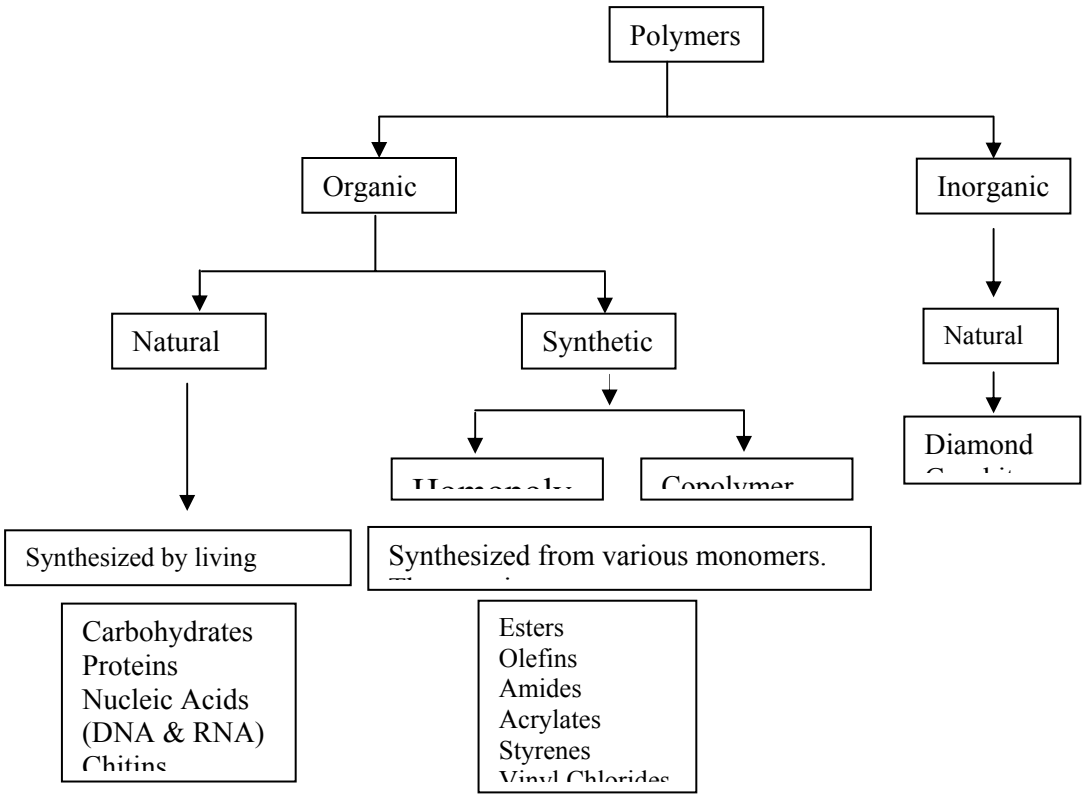
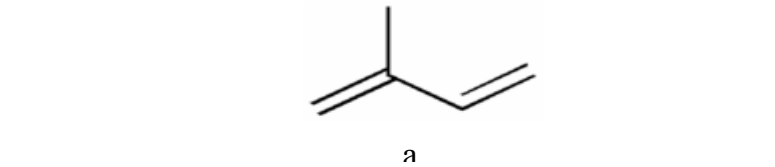
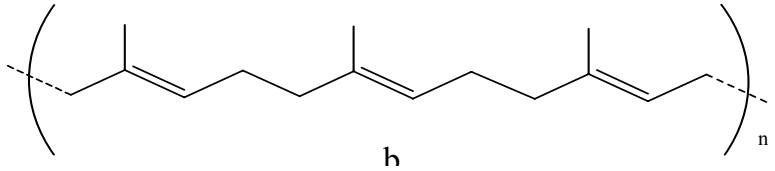


Fig III: Polymers can be classified into organics and inorganics. Further classification is done based on their source: synthetic and natural.

The only way to get the desired type and grade of organic polymers from natural sources is by way of bringing modifications in the structure of nucleic acids of the species. Natural polymers are very important for the existence of life as they support the living species. The natural polymers have been exploited for different uses-both industrial and household.



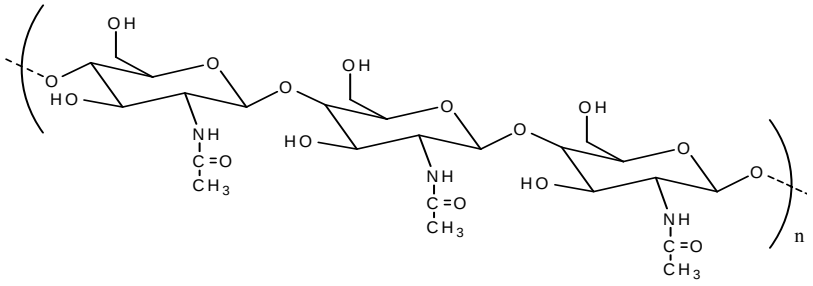
a



b

Rubber

Fig IV: Structure of (a) Isoprene unit which is also the monomer unit for rubber (b) Rubber which is a product (polymer) based on isoprene unit.



Chitin

Fig V: Structure of an organic polymer, Chitin, which is produced by certain marine species and finds applications in various industries

Natural Polymers

All living beings are composed of organic polymers, which not only provide structural materials for the maintenance of life functions but also participate in carrying out the life function itself. Cellulose , is a polysaccharide and a natural polymer whose monomer units are individual sugar molecules. In all types of wood, cellulose is accompanied by lignin, a second polymer, which shows much less regularity than cellulose. Another important class of natural polymers is rubber, which consists of terpenes such as isoprene **(Fig VI)**.

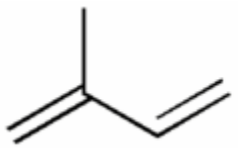


Fig VI: Structure of isoprene (a terpene), which is responsible for the formation of rubber. It is the monomer unit for rubber.

The monomeric units of proteins are amino acids, which are relatively small molecules containing amine and carboxylic acid groups. Other important natural polymers, are the polymers of glucose called starch. They are widely distributed in plants and play a wide role as food for animals of all kinds. Starches are different from cellulose since the individual monomeric units are joined in the molecules. Chitin is composed of long chains of glucose molecules that have been modified by acetylated amino groups; the molecular weights of a typical chitin polymer is around 100, 000.

The formation of cellulose, lignin and terpenes is the part of the process, which is responsible for the growth of the plant species. Since all these natural polymers are of great significance for the humans, the plants are grown for this purpose. As the plants consume carbon dioxide for their growth, growing plants also has an impact on environment and ecology. The requirement of starch and protein is met mainly by agriculture.

The natural polymers are of both inorganic and organic types. While the organic polymers are formed by the living systems and are renewable, the inorganic polymers are as a result of certain chemical transformations in various inorganic compounds occurring in earth and they are not renewable.

Inorganic polymers

The naturally occurring inorganic polymers are found in nature in the mineral resources of the earth. Various metallic and non-metallic resource elements have the tendency to bond with each other in polymeric structure forms. Such polymers are formed mainly because of the chemical nature and the conditions of pressure and temperature under which various elements exist and undergo transformation over the years.

The most interesting inorganic polymers are a class of materials known as silicates. The building block of all kinds of silicates is based on silica (SiO_2). SiO_2 exists in a tetrahedral form and depending on the nature of the counter ions, the fashion in which the silicate structures are arranged with the counter ions and the manner in which the different silicates are arranged, various types of polymeric forms of a class of chemicals known as silicates are formed naturally. The wide range of applications makes silicates an important class of inorganic polymers.

Diamond is a good example of an inorganic three-dimensional polymer structure of carbon atoms joined together by single bonds **Fig VII**. Graphite consists of two-dimensional polymeric layers of carbon atoms joined together by alternative single and double bonds **Fig VIII**.

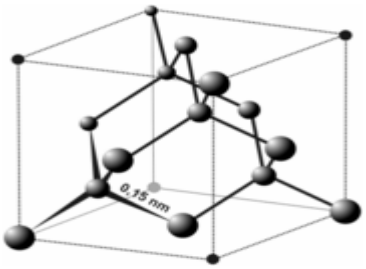


Fig VII: Structure of three-dimensional polymer-Diamond, in which carbon atoms are joined together by single bonds. It has a tetrahedral geometry where each carbon atom is bonded to 4 other carbon atoms.

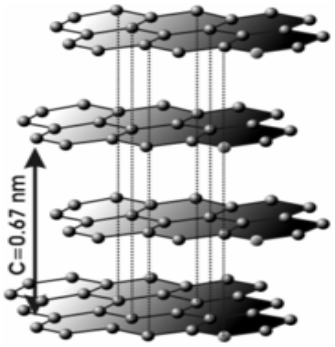


Fig VIII: Structure of two-dimensional polymer-Graphite, in which carbon atoms are joined together by alternate single and double bonds. It has a square planar geometry where each carbon atom is bonded to 3 other carbon atoms.

Organic Polymers

There are numerous examples of organic polymers, which we encounter, in our daily life. Some important ones are discussed here below:

Carbohydrates: Polysaccharides are high molecular weight polymers of monomeric sugars and have molecular weights that may vary from a few thousands to several millions, e.g. Starch ($(C_6H_{10}O_5)$) which occurs in all green plants.

Commercial sources of starch include maize, wheat, barley, potatoes and sorghum. Starch has two fractions –

β-amylose **Fig IX** or amylopectin and α-amylose **Fig X**.

β-Amylose contains 80 – 90 % of starch molecules while α - amylose is 10 – 20% of starch molecules. α -amylose consists of unbranched chains with molecular weights between 10,000 – 1,000,000 and amylopectin consists of branched chains having a molecular weight between 50,000 – 10,000,000. Starch is a good source of food for humans.

Cellulose is a polymer of β -D- glucose **Fig XI**. Cellulose is a constituent of plant cell wall and also occurs in certain animal tissues. It is the most widely distributed organic compound. The main source of cellulose is cotton and wood. The cellulose is a good source of food for animals, the humans don't have the enzymes which can digest β -D- glucose and hence, cellulose in their stomach.

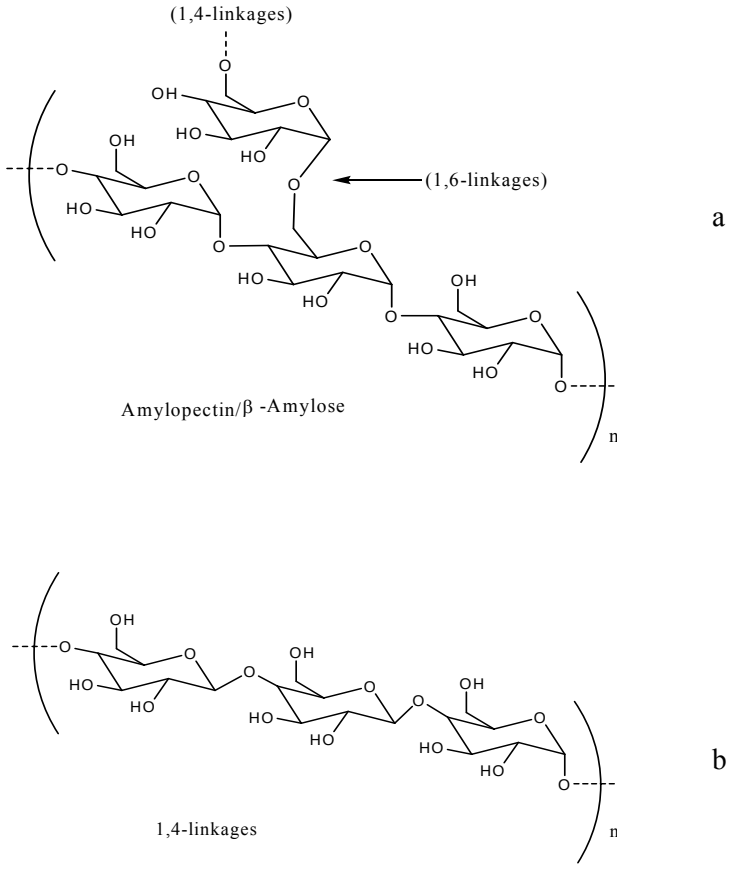


Fig IX: (a) β-amylose unit of starch, which has 1,4 and 1,6 linkages. 1,4 linkage is intermolecular (chain formation) whereas 1,6 is intramolecular (cross-linking) linkage. (b) Figure depicting 1,4 linkage in α-amylose unit.

Proteins: Proteins are polymers of the monomer amino acids. There are a total of 20 amino acids, which are linked by amide linkages to form proteins. Proteins have molecular weights above 10,000 **Fig XII**.

Terpenoid: Terpenoids are polymers of isoprene units. Rubber, an important terpenoid obtained from latex, consists of isoprene units as the monomer and is obtained from inner bark of many tropical trees **Fig XIII**.

Polysaccharide : Polysaccharides are the polymers based on sugar molecule as monomer. Chitin is a polysaccharide that is found in the shells of crustaceans. The structure is similar to that of cellulose except that N- acetyl glucosamine replaces β– D glucose.

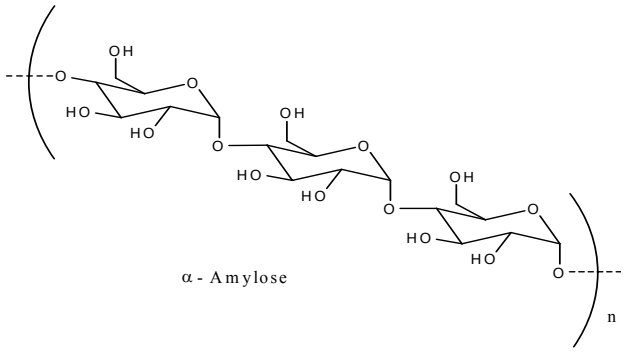


Fig X: α-amylose unit of starch. It is a straight chain with molecular weight between 10, 000-1, 000, 000.

Nucleic acids: Nucleic acid is made up of the monomer nucleotides. A nucleotide has a sugar group (DNA has deoxy-ribose and RNA has ribose .phosphate group and a base (purine or pyrimidine) **Fig XIV-XVII**.

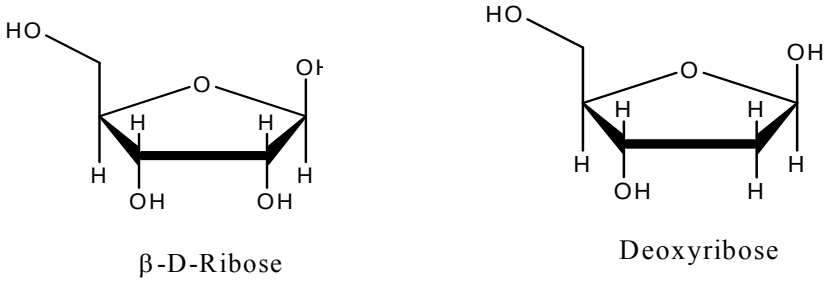


Fig XIV: Structures of sugar molecules present in DNA & RNA. β-D Ribose is present in RNA and deoxyribose is present in DNA.

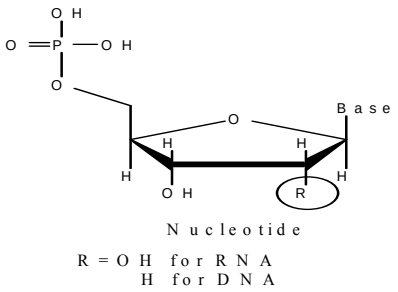


Fig XV: Basic structure of a nucleotide consisting of a sugar molecule, a phosphate group and a base.

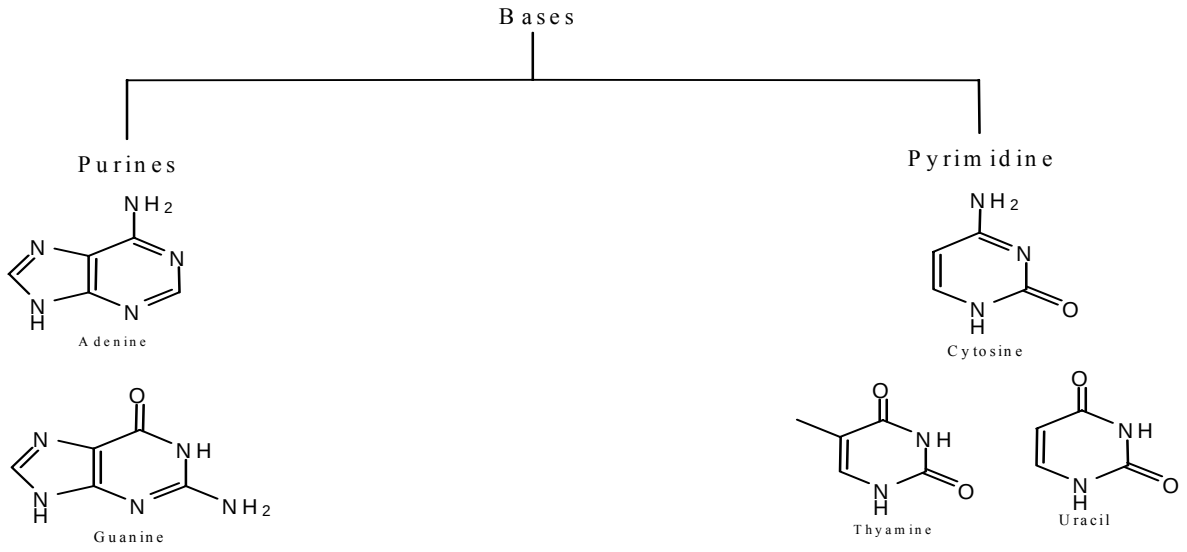


Fig XVI: Picture depicting bases (purines or pyrimidines) involved in the structure of DNA and RNA.

Synthetic polymers

All the man made polymers are referred to as synthetic polymers. In the beginning of the 20th century, when the structure and character of the most important natural polymers-cellulose,

proteins, and rubber were elucidated, attempts were made to synthesize similar polymers. These attempts led to the development of a large number of polymers classified as synthetic polymers, which in turn led to the discovery of an amazing variety of industrial applications of polymers as fibers, plastics, synthetic rubbers, coatings and adhesives, foam, etc. Because of their physico-mechanical behavior, polymers are also known commonly as plastics **Fig XVIII** . Synthetic polymers are extremely versatile, and serve as a good alternative to conventional materials. For example, polycarbonates are a group of synthetic polymers replacing glass in applications such as spectacle lenses.

On heating, the polymers change their forms and infact the unique thermal behavior of polymers has been the main reason for the wide acceptability of polymers (plastics) in different industrial applications.

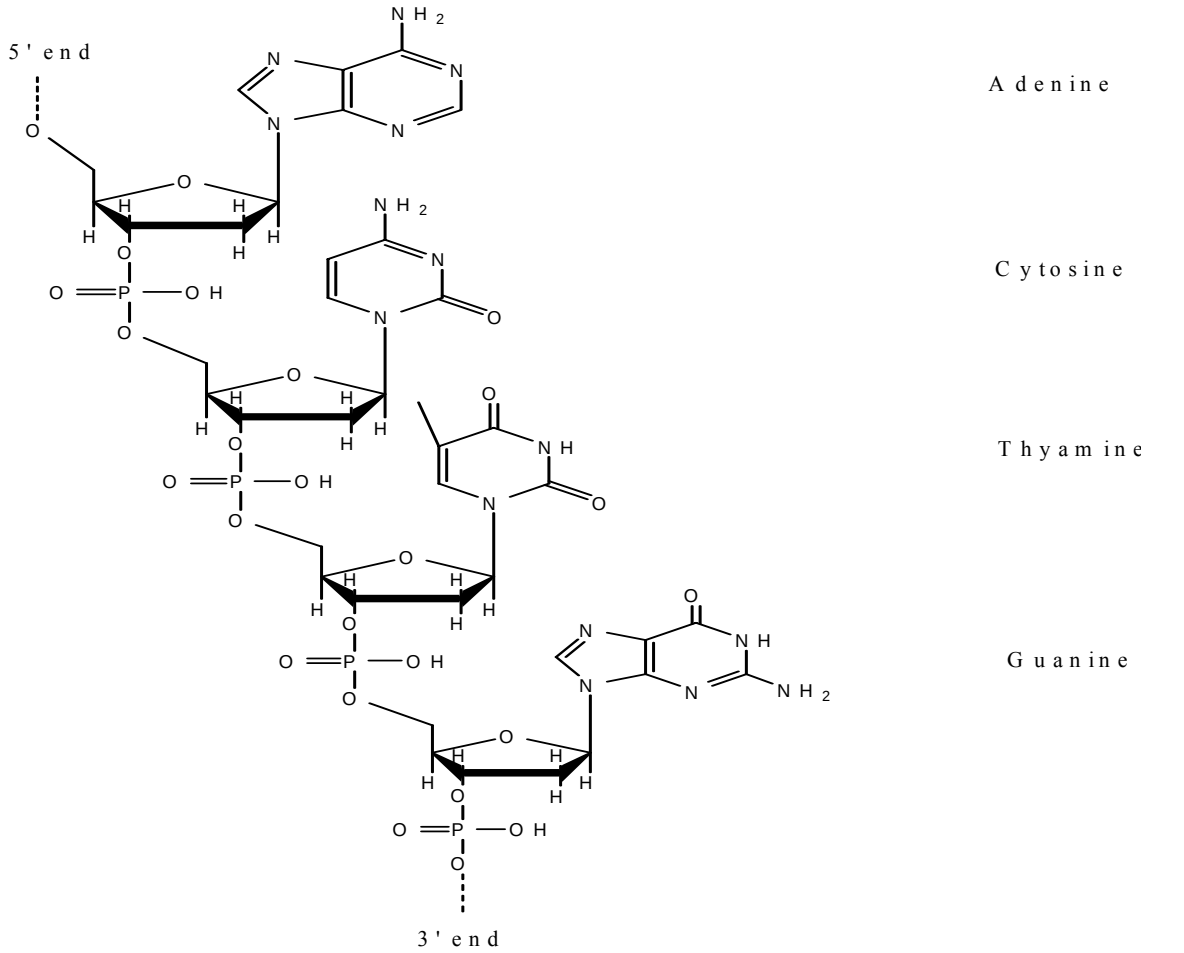


Fig XVII: Structure of DNA ACTG strand where nucleotides are attached by 5'-3' linkages.

Synthetic polymers generally are classified into two broad groups in accordance with their behavior upon heating.

1. Polymers that can be repeatedly melted and solidified (without damage) are said to be thermoplasts;
2. Polymers that solidify once but will not melt again without damage to their structure are said to be thermosets.

a

b

c

Fig XVIII: Various applications of synthetic polymers like (a) Plastics (b) Coating for wheels and (c) Rubbers for tyres

Thermoplastics: Thermoplastics, as the term suggests, can be softened repeatedly without undergoing a change in chemical composition. Thermoplastics have linear structures where the polymer chain remains linear and separates out after molding; remolding can be achieved repeatedly. Remouldability of such polymers makes them a preferred material for various applications. On heating, these polymers change their form and this unique thermal behavior of polymers (plastics) has led to their different industrial applications.

Examples of thermoplastics are polyethylene, teflon, polystyrene, polypropylene, polyester, polymethyl methacrylate, polyvinyl chloride, nylon, silicone, fiberglass, etc. Since all these polymers have a very stable structure, the waste of such polymers can also be a valuable material for developing value-added products.

Thermosets: Thermosets are cross - linked structures where linear chains are joined irreversibly during molding into an inter-connected molecular network and cannot be remolded. Such cross - linkings can be achieved by heat, chemical agents, radiation or by a combination of all of these. Examples are vulcanized rubber, bakelite, kevlar, epoxy polymers, etc.

Based on the type of monomer involved, polymers are generally classified according to the chemical character of their monomers. The commonly known polymers, as shown below, are classified in different groups based on their chemistry.

Esters

Esters are formed by condensation of an acid and alcohol with loss of a water molecule. When such condensation reactions are used for formation of polymers, the method is called condensation polymerization. Each molecule has two ends, and if both the ends have alcoholic group or alcohol and acid group, then esterification reaction will lead to polymer formation formation. These polymers have monomeric units linked by ester linkages. Polyesters, therefore,

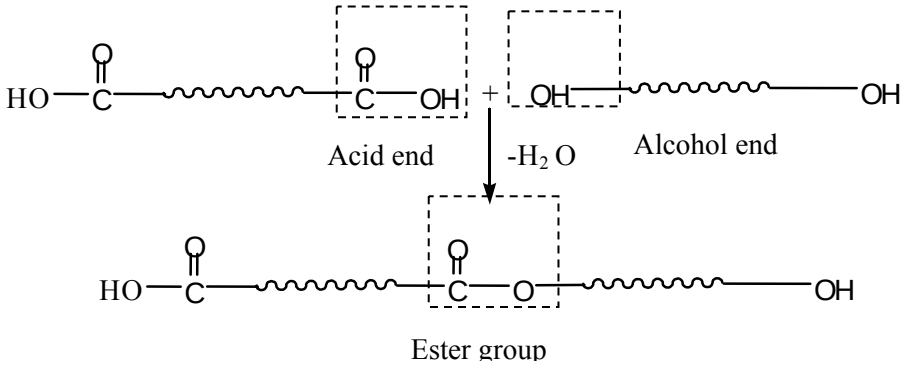


Fig XIX: Ester formation by the reaction of an acid group and an alcohol group where each end of the ester molecule has reactive sites which leads to polymerization.

can be designed by taking the base materials; one having two hydroxyl groups while the other having two carboxylic groups **Fig XIX**. Example polyethylene terephthalate is formed by the condensation reaction of an acid (terephthalic acid) and a hydroxyl group (monoethylene glycol).

Olefins

These are involved in addition polymerization in which no neutral small molecules are released during the reaction **Fig XX (a) - (f)**.

Amides

Amides are formed by the reaction between a COOH group and an NH_2 group, leading to the loss of a molecule of H_2O. This condensation reaction can be used to form polymers where monomers are linked by amide groups. For example, Nylon 6,6 is formed from adipic acid and 1,6-hexamethylene diamine and Nylon 6 is made from caprolactam **Fig XXI (a) - (b).**

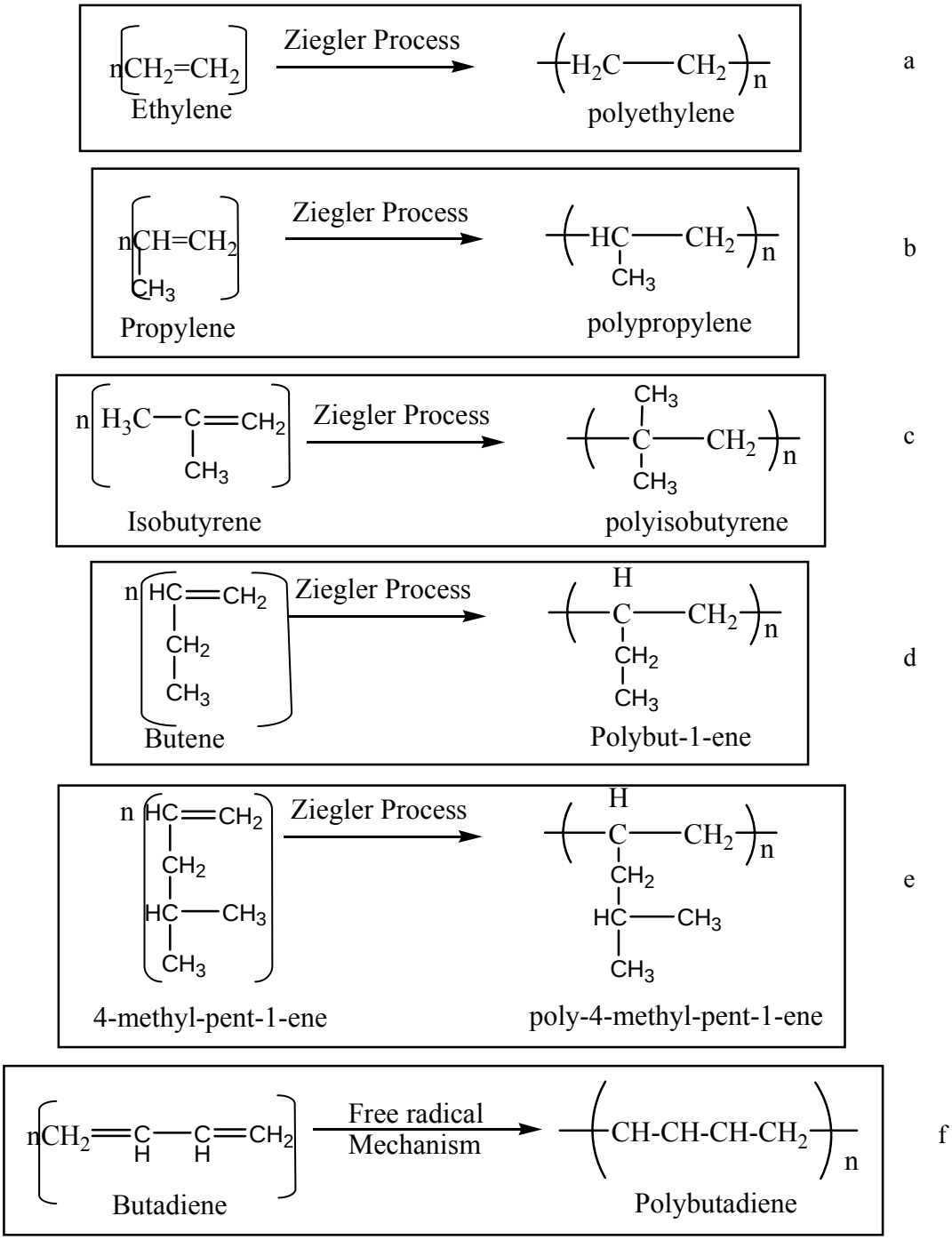


Fig XX (a)- (f): A few examples of addition polymerization reactions in which no small neutral molecule is released during the reaction.

Acrylates

Acrylates have two functional groups- a carboxylate and a double bond. The double bond is responsible for polymer formation by the method of addition polymerization to form polyacrylates **Fig XXII (a) – (b).** Acrylic fibers show excellent resistance to light and to weather, and resemble wool. Polyacrylates are also used in super-glues.

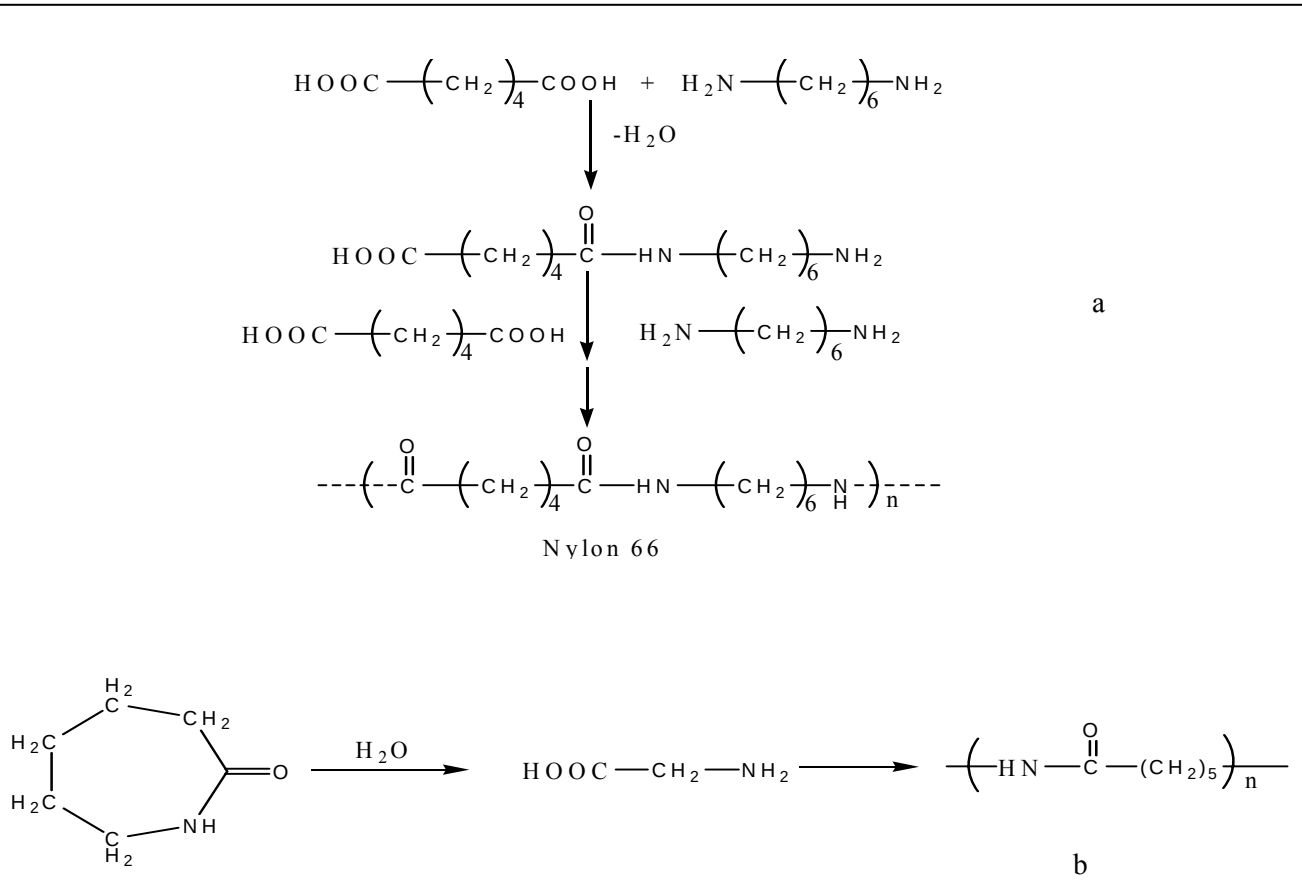


Fig XXI: (a) Reaction of adipic acid and hexa methylene diamine to form Nylon 6,6. The product consists of an amide linkage between –COOH group and the $–NH_2$ group. (b) Reaction of the hydrolysis of caprolactum to yield Nylon 6.

Styrenes

Styrene has a double bond on the alkyl chain and this undergoes addition polymerization to form polystyrenes **Fig XXIII.** The monomers having styrene in their structure form polystyrene type polymers.

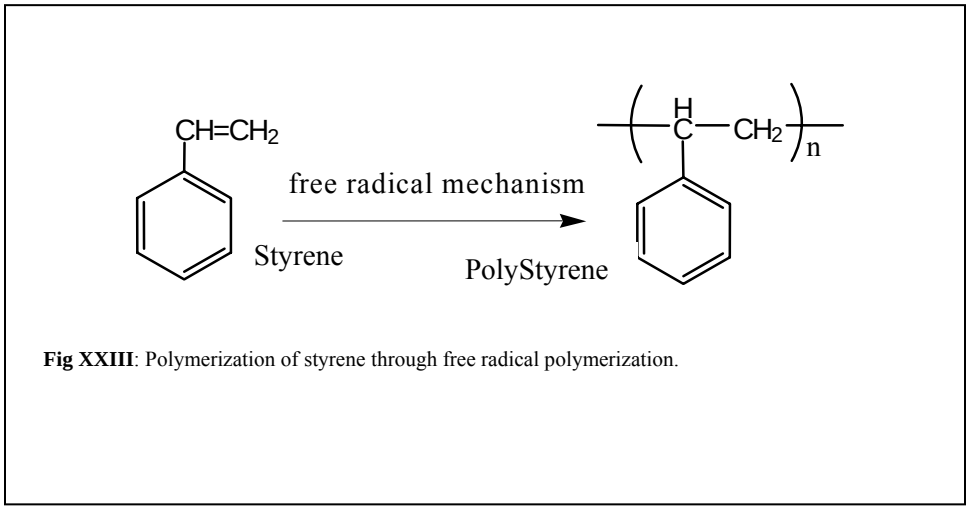


Fig XXIII: Polymerization of styrene through free radical polymerization.

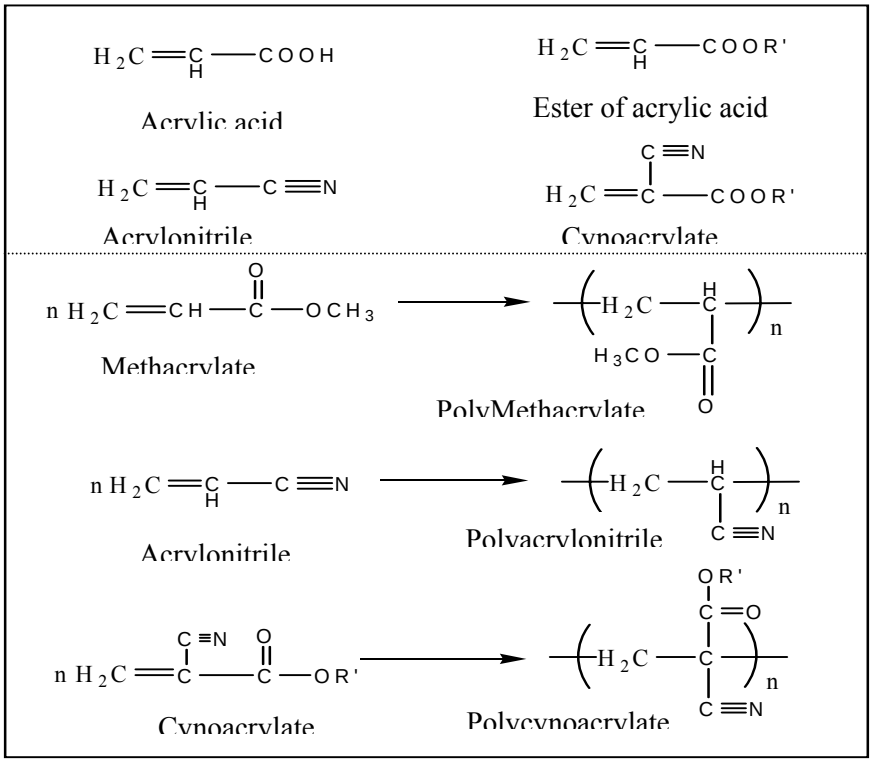


Fig XXII: Structures of (a) acrylates of various types and (b) the reactions for the synthesis of different polymeric acrylates.

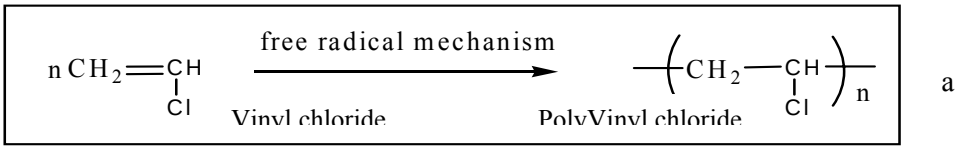
Vinyls

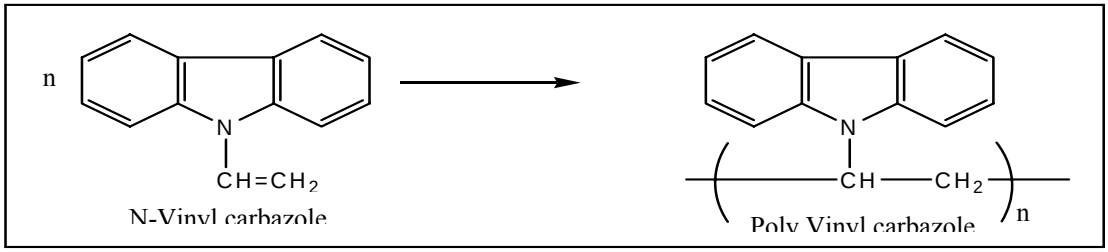
Vinyl group can be made to undergo addition polymerization to form polyvinyl chlorides (PVC) from vinyl chlorides **Fig XXIV (a)-(d).** One can also develop poly-vinyl alcohols, but unlike PVC, they are not made from vinyl alcohol. Vinyl alcohol is very unstable and thus addition polymerization of vinyl alcohol is not possible. However, vinyl acetate (ester of vinyl alcohol and acetic acid) is stable and can be made to undergo addition polymerization. Since vinyl alcohol is unstable, vinyl acetate is prepared from ethylene oxide and acetic acid.

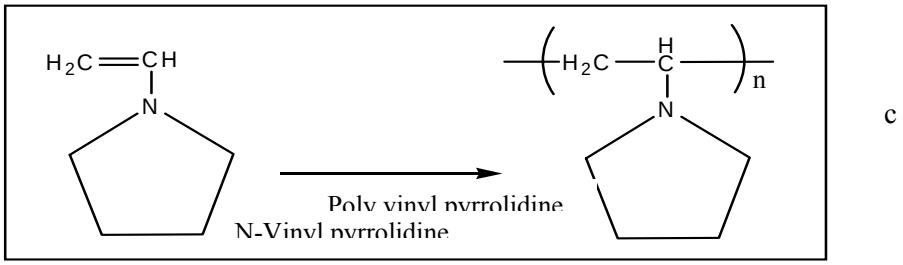
Fig XXIV (e). Polyvinyl alcohol is made from polyvinyl acetate by alcoholysis. When methanol is added to polyvinylacetate, trans-esterification takes place and methyl acetate (the new ester) is formed along with polyvinyl alcohol **Fig XXIV (f)**.

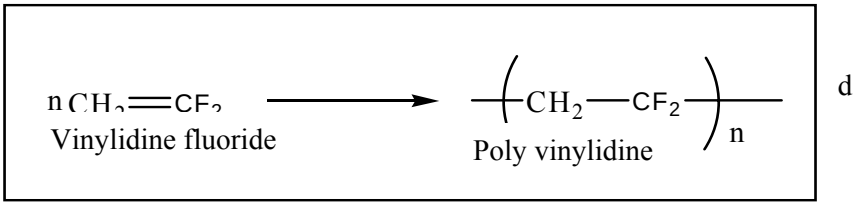
Siloxanes

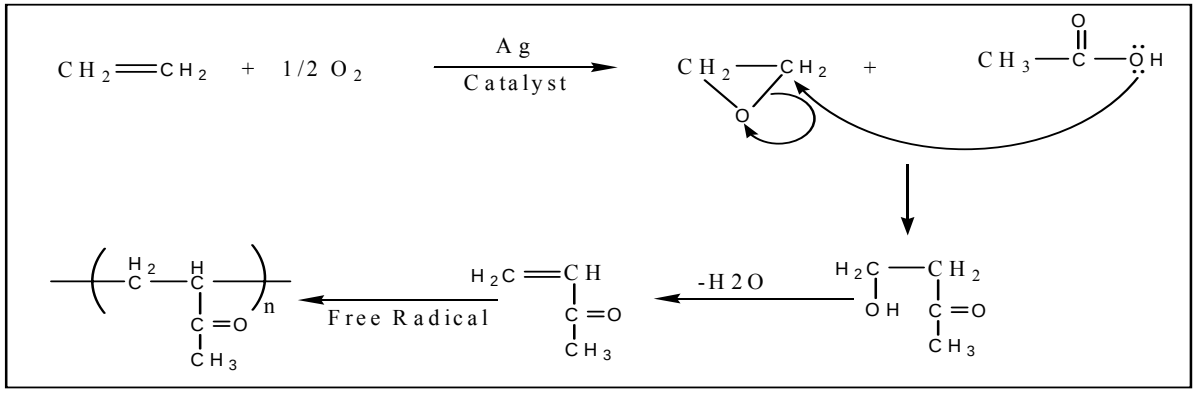
These are also condensation polymers and are formed as shown in **Fig XXV.**











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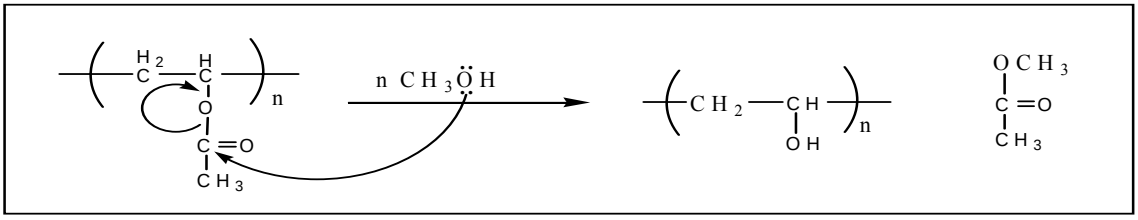

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Fig XXIV (a)-(f): Polymerization of vinyl groups to polyvinyls through free radical polymerization.

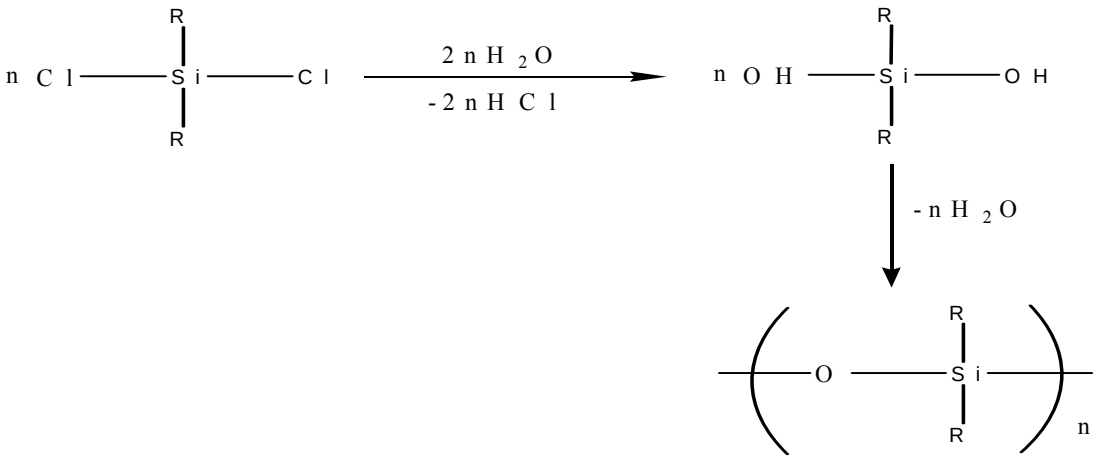


Fig XXV: Figure depicting condensation polymerization of siloxanes.

Elastomers

Elastomers are a class of polymers having properties similar to natural rubber in terms of softness, flexibility and resilience. Elastomers are thermoplastic in nature and are known as thermoplastic elastomers.

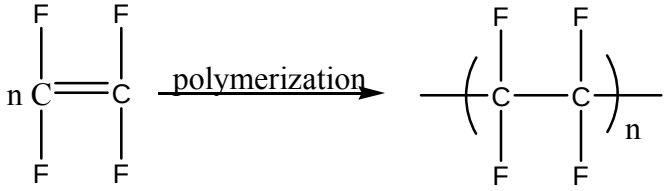
Thermoplastic elastomers are multiphase compositions in which the phases are intimately dispersed. The phases are chemically bonded by block or graft co-polymerisation.

A simple structure is an A-B-A block copolymer where A is a hard phase and B is an elastomer. A can be a thermoplastic polymers such as polypropylene, polystyrene and polymethylmethacrylate. B can be any polymer regarded as an elastomer such as polyisoprene, polybutadiene, polyisobutylene and polydimethyl siloxane.

Polymerization

The process of making polymers and in other words the linking of small molecules (monomers) to make larger molecules (polymers) is called polymerization. In order to form polymers, monomers must either have reactive functional groups or have double (or triple) bonds for the necessary linkages between repeating units. Process of polymerization requires that each small molecule has at least two reaction points or functional groups so that the linkages between molecules become possible to form long chain structures.

It must be noted that during the polymerization, a polymer is formed by the repetition of small simple chemical units, also called the repeating units, joining together. For example, the n number of monomer tetra fluoroethylene (TFE) join together to form poly tetra fluoro ethylene (PTFE) having the molecular weight equal to n number of tetrafluroethylene.



Tetrafluoroethene Poly (tetrafluoroethene)

Classification of polymers

Besides the classification based on their chemistry, the polymers can also be classified based on their process of manufacturing. There are three major types of polymerization processes, by which polymers may be produced, synthetically, starting from simple materials. These techniques are:

1. Addition polymerization or Chain growth polymerization
2. Condensation polymerization or Step Growth polymerization
3. Rearrangement polymerization

Addition Polymerization or Chain Growth Polymerization : When the monomer molecules add to each other to result in growing chains of polymer without the elimination of any part of the monomer molecule is termed as addition polymerization. A monomer having a double bond is

induced to break the double bond and the resulting free valencies are able to join up to other monomer molecules. Addition polymers formed this way by the reaction of monomer with a reactive center are also known as chain growth polymers. These polymers grow to high molecular weight at a very fast rate and thus, form high molecular weight polymers.

Polyethylene made by the polymerization of ethylene, polystyrene made by the polymerization of styrene and polyvinyl chloride made by the polymerization of vinyl chloride are examples of addition polymerization. In this type of polymerization, unsaturated carbon-carbon bonds as explained in **Fig XXVI** are opened up.

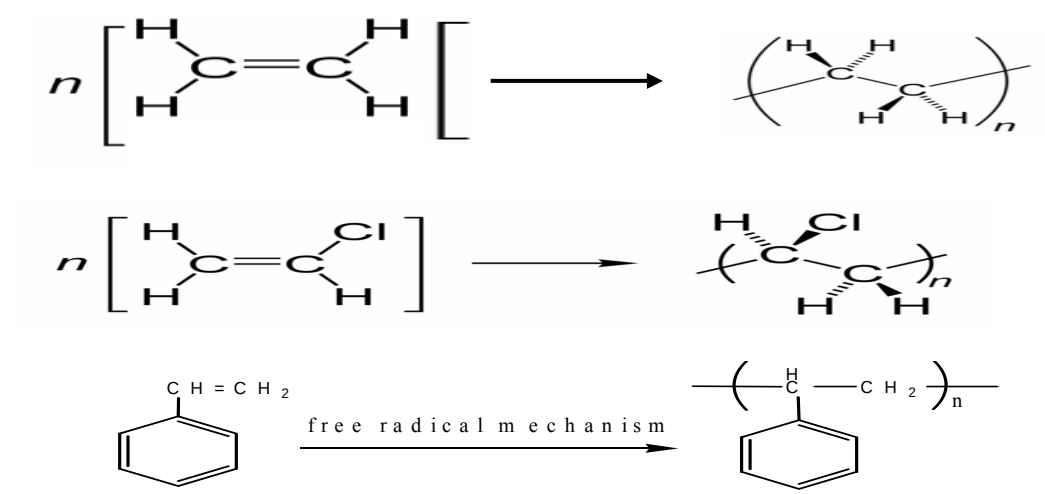


Fig XXVI (a)-(c): Examples of Addition polymerization where unsaturated carbon-carbon bonds can be opened up by free radical mechanism.

Polymerization of formaldehyde to polyformaldehyde is another kind of addition polymerization in which the carbon-oxygen bonds are opened up.

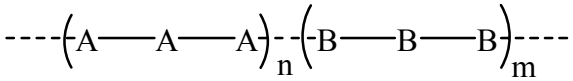
Another kind of addition polymerization is one in which monomers containing more than one double bond such as conjugated dienes are polymerized in such a way that it generates long chain molecules with residual double bonds in the chain.

Ring opening reactions such as the polymerization of ethylene oxide to polyethylene oxide is another example of addition polymerization. In both these cases, the epoxy ring opens to produce active sites which join to result in polymer chain. The addition polymerization involves three steps i.e initiationof chain, growth of chain and then termination of the chain. In this way, the monomers add to each other during the chain –growth step and after the termination of chain, further addition stops. The molecular weight and molecular weight distribution of the polymers vary depending upon the kinetics and energy involved in each step.

By controlling the three steps of the cxhain polymerization, one can infact achieve the desired molecular weight distribution. If the polymer chains are made to grow at a contant rate, then the

polymer chains would have a narrow range of molecular weight or low polydispersity. This is possible by making the rate of chain initiation much larger than the rate of chain propagation and by rendering the chain termination almost absent. This type of chain polymerization is also called as living polymerizationan it has become a popular method to produce block co-polymers which are made up of more than one monomer.

Block copolymers can be synthesized in stages where each stage containis a different monomer. Additional advantages are i) predetermined molar mass of the desired polymer ii) control over the end groups of the polymer at each end. Block copolymers can be produced in two ways: (i) have a block chain of desired length based on one monomer and then attaching the other block chain with desired length based on another monomer and (ii) build the polymer chain with both monomers taken together and made to produce polymer of desired chain length with the monomers arranged in random manner. Such polymers are also called as random block copolymers.



Continuous type block copolymer

Random type block copolymer

In chain growth polymerization, the monomer polymerizes in the presence of compounds called initiators. The initiator continually generates growth centers in the reaction mass, which add on monomer molecules rapidly. It is this sequential addition of monomer molecules to growing center that forms chain polymer. Growth centers can be either ionic (cationic or anionic), free-radical or co-ordinational in nature depending upon the kind of initiator system used. Based upon the nature of the growth of the centers, chain growth polymerization is further classified as follows:

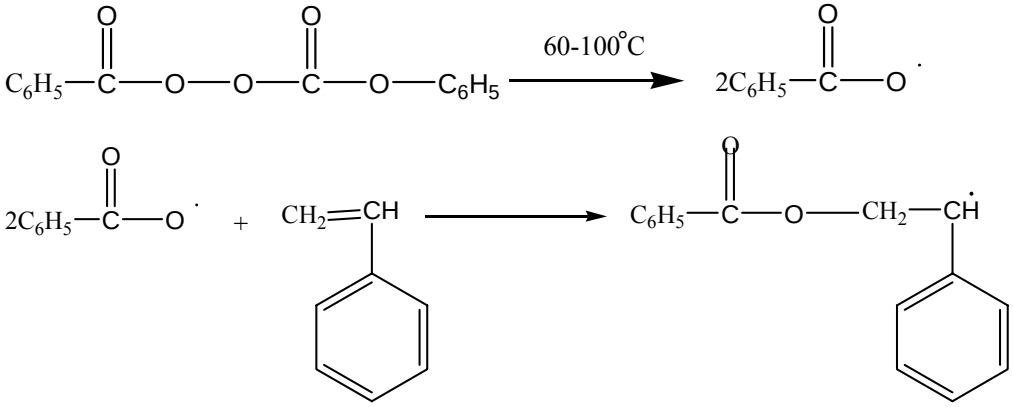
- Free radical polymerization
- Ziegler - Natta Polymerization
- Cationic polymerization
- Anionic polymerization

Polymerization is categorized into two types of polymerization, according to the nature of the growing polymer centers, as:

1. Radical polymerization
2. Cationic polymerization
3. Anionic polymerization
4. Co-ordination or stereo-regular polymerization

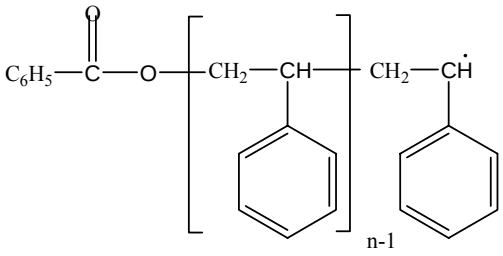
Free Radical Polymerization: Most synthetic plastics and elastomers and some fibers are prepared by free radical polymerization. **Table I** represents some industrially important addition polymers. The free radical mechanism can be divided into three stages. As is the case with other chain reactions, free radical polymerization is a rapid reaction which consists of the characteristic chain reaction steps: initiation, propagation and termination. Free radical initiators are produced by hemolytic cleavage of covalent bonds and their formation is dependent on high-energy forces.

Initiation : Initiation is the creation of free radicals necessary for propagation.. A material which can be made to decompose into free radicals on warming, or in the presence of a promoter or by the irradiation with radiations of different energy from electromagnetic spectrum, example, ultra-violet light, is added to the monomer and radicals are formed having unpaired electrons. Such materials are known as initiators. For example benzoyl peroxide and azo bis iso butyro nitrile acts as initiators **(Fig. XXVII-XXVIII)**. The initiation step consists of two elementary reactions. For example, benzoyl peroxide on heating decomposes to give benzoyl oxy radicals.



There are two types of radicals in the reaction mass:

1. Primary radicals (for e.g. $C_6H_5COO^{\cdot}$) which are generated by the initiator molecules
2. Growing chain radicals of monomer molecules



Reaction between a primary radical and a polymer radical would make polymer radicals unreactive by destroying their radical nature. Such reactions are called termination reactions. There are thus five kinds of species in the reaction mass at any time: initiator molecules, monomer molecules, primary radicals, growing chain radicals and terminated polymer molecules.

During initiation, the homolytic dissociation of an initiator species I to give a pair of radicals $R^{\cdot}$ takes place. The initiation step is therefore, considered to involve two reactions:

$$I \xrightarrow{k_d} 2\,\dot{R}$$

where k_d is the rate constant for the dissociation of the initiator molecule. The second step of initiation involves the addition of the initiator radical to the first monomer molecule to produce the "real" chain initiating species (radicals) $M_1^{\cdot}$:

$$R + M_1 \xrightarrow{k_i} \dot{M}_1$$

Here, k_I is the rate constant for the initiation step.

Let us understand this in the case of manufacture of polyethene. In this case the ethylene molecule has two pairs of electrons held securely between the two carbons of a double bond: one of them in a sigma bond whereas the other is more loosely held in a pi bond. The free radical uses one electron from the pi bond to form a more stable bond with the carbon atom. The other electron returns to the second carbon atom, turning the whole molecule into another radical in the manner as explained above.

The rate of formation of radicals will depend upon a number of factors like concentration of initiator, temperature, and the presence of other agents.

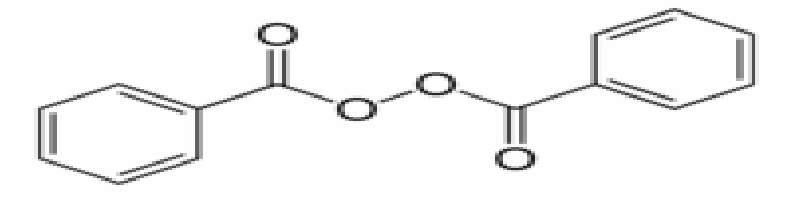


Fig XXVII: Benzoyl peroxide-an initiator for free radical reactions.

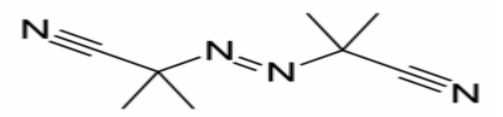
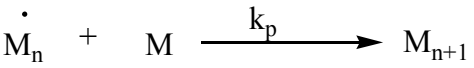


Fig XXVIII: Azo bis iso butyro nitrile- An initiator for free radical reactions

➢ *Propagation*

Propagation is the rapid reaction of this radicalised ethylene molecule with another ethylene monomer, and the subsequent repetition to create the repeating chain. This reaction repeats itself so that several thousand monomer units are joined together, leading to a longer chain free radical. As propagation continues and each monomer unit is added, the radical has the same identity as the radical before except that it is larger by one unit.



Here, $M_n^{\cdot}$ is the radical which is responsible for propagation, n is the number (the minimum value of n can be 1) of monomer units in the radical and k_p is the rate constant for the propagation step.

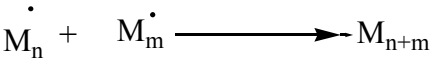
Propagation with growth of the chain to higher molecular weight polymer takes place very rapidly. But at some point the propagating radical at the end of the polymer chain stops growing and finally, it terminates.

➢ *Termination.*

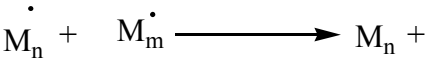
Termination occurs when a radical reacts in a way that prevents further propagation. The most common method of termination is by coupling where two radical species react with each other forming a single molecule. Another less common method of termination is disproportionation where two radicals meet, but instead of coupling, they exchange a proton, which gives two terminated chains, one saturated and the other with a terminal double bond.

Termination can be achieved in a number of ways, including:

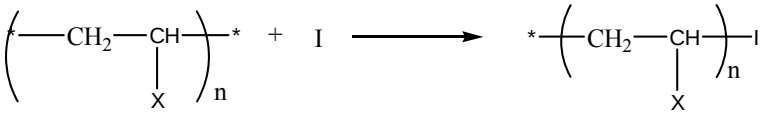
1. Mutual combination of two growing radicals



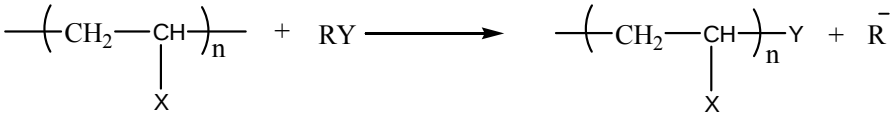
2. Disproportionation between growing radicals



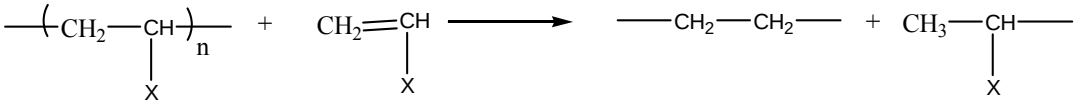
3. Reaction with an initiator radical, for example in the case of ethylene chloride:



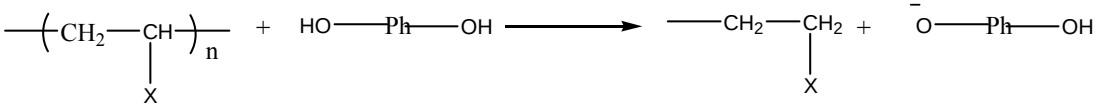
4. Chain transfer with a modifier, for example, in the case of ethylene chloride



5. Chain transfer with monomer, for example, in the case of ethylene chloride



Reaction with a molecule to form a stable free radical, for example, termination for polyethylene chloride by hydroquinone



Example of Free radical polymerization

The polymerization of vinyl chloride is a typical example of free radical polymerization. Vinyl chloride molecules contain two carbon atoms, three hydrogen atoms, and one chlorine atom. In vinyl chloride, the bond between the two carbons is a double bond consisting of two shared pairs or four electrons.

During free radical polymerization, one of the two bonds between the two carbon atoms ruptures, leaving one unshared electron on each carbon atom forming the vinyl chlorides free radical. If two such free radicals meet, they can form a dimer with a new covalent bond linking the two vinyl chlorides:

This dimer can react with another vinyl chloride to form a trimer and so on to form polyvinyl chloride (PVC):

Co-ordination or stereoregular polymerization

Zieglar natta polymerization is also known as co-ordination of stereo-regular polymerization carried out in the presence of special catalyst or catalyst systems called Zieglar Natta catalysts.
A mixture of $TiCl_3$ and $AlEt_3$ form Zieglar Natta catalyst for the polymer of propylene. Zieglar Natta polymerization involves the rapid polymerization of olefins, using the special Zieglar Natta catalysts, under mild conditions in the presence of transition metal compounds. In fact, polymers with specific configuration schemes cannot be obtained by normal polymerization, special catalysts called Zieglar Natta catalysts are used for producing polymers with specific configuration.

Ziegler-Natta catalysts generally consist of a metal organic compound involving a metal from groups I - III of the periodic table, called co-catalyst, such as $AlEt_3$, Al $(n\text{-}C_6H_{12})_3$, Al $(C_2H_5)_2Cl$, and a transition metal compound (from groups IV - VIII), called as catalyst, such as $TiCl_3$, $TiCl_4$, $TiCl_2$, VCl_4. The metal organic compound acts as a weak anionic initiator, forming a complex. Polymerization proceeds by a process of insertion. The transition metal ion **(Fig XXIX),** for example, Ti connects to the end of the growing chain and simultaneously coordinates the incoming monomer at a vacant orbital site. Two general mechanisms viz mono-metallic and bi-metallic have been proposed . For stereoregular polymerization, it is necessary to determine the activity of the different combinations of catalyst-co-catalyst systems in polymerizing a particular monomer.

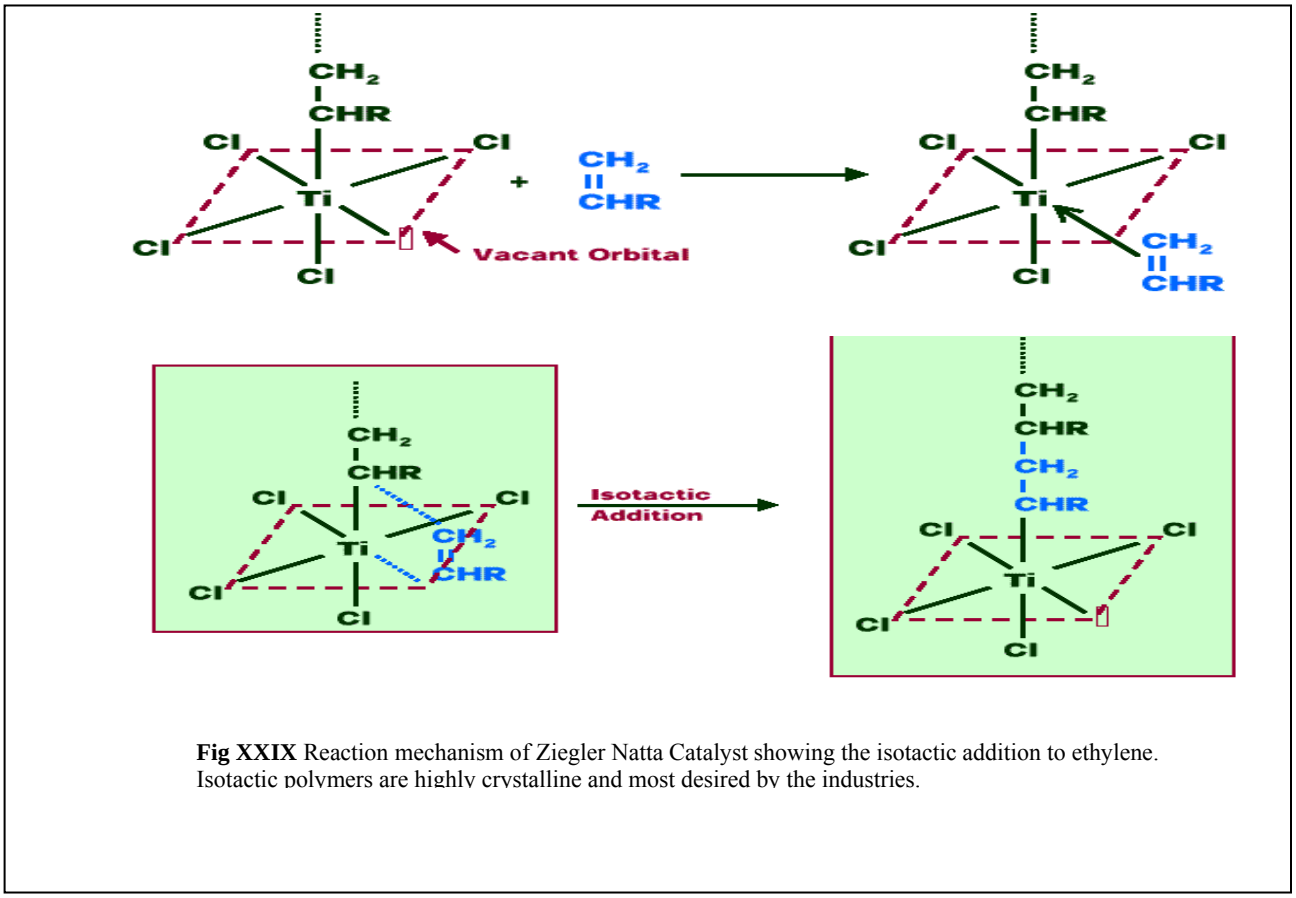


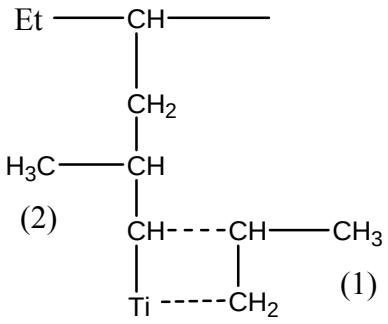
Fig XXIX Reaction mechanism of Ziegler Natta Catalyst showing the isotactic addition to ethylene. Isotactic polymers are highly crystalline and most desired by the industries.

Isotactic placement can then occur if the coordinated monomer is inserted into the chain in such a way that the growing chain remains attached to the transition metal ion in the same position.

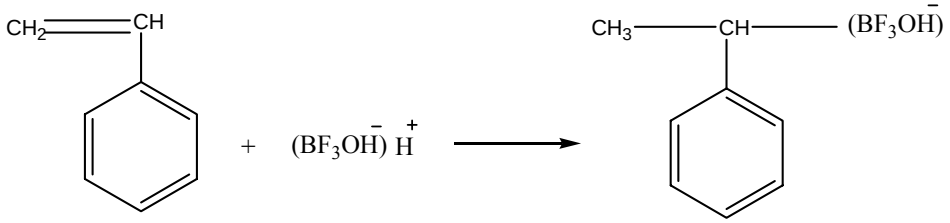
If the chain becomes attached to the transition metal ion in the position of the orbital that was initially vacant, syndiotactic addition will occur. This becomes more favored at lower temperatures, but vinyl monomers usually form isotactic chains with these catalysts. Because of the heterogeneous nature of the geometry of the catalyst surface atactic and stereo block polymers can also be formed. Zieglar Natta polymers are easily controlled and less expensive; precaution must be taken to avoid fire because co-catalysts are pyrophoric in nature. During is employed in Zieglar Natta catalyst and it is dispersed and polymerization starts as soon as the gaseous monomer is introduced. In the case of liquid monomers, solvent is not necessary. polymerization, the monomer can be either a liquid or a gas. If the monomer is a gas, a solvent medium

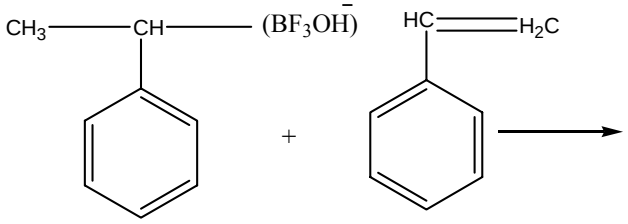
Zieglar Natta catalyst also contain supports such as MgCl2 andinert carriers such as silica, alumina and various polymers.

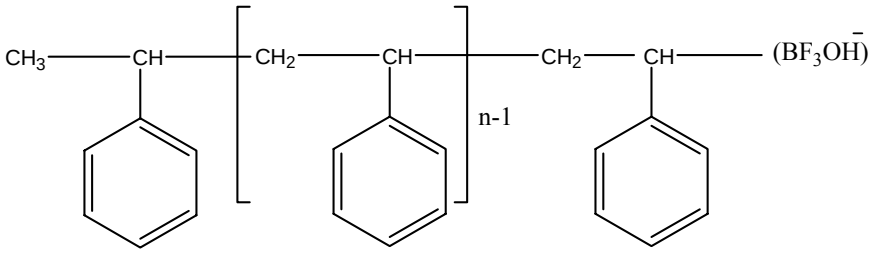
Stereo-regulation of polymers occurs as follows



In the activated complex, there are two kinds of interactive force (a) steric hindrance between methyl groups (1) and (2) and (b) interaction between methyl groups and chlorine atom. If the interactive forces between ligands and substituent of the adsorbed molecule is not too large, the addition of the CH_3 group of the monomer to the propagating chain occur such that it minimizes the steric hindrance between itself and CH_3 group (2) giving a syndiotactic chain. If the interaction between CH_2 (1) and Cl atom is large, it can lead to the formation of a isotactic chain.



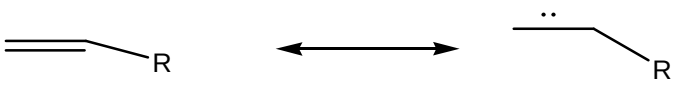




Ionic vinyl polymerization

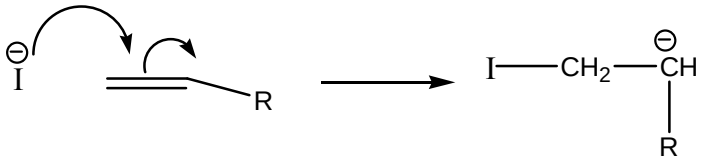
Ionic vinyl polymerization is very similar to free radical vinyl polymerization. The only difference is in the "flow" of the electrons during propagation.

A double bond equals a single bond plus two more electrons.

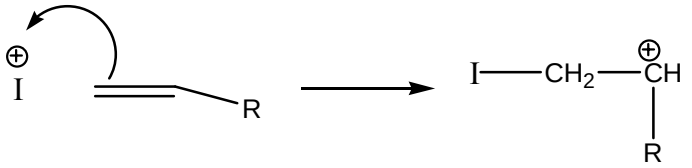


In *free radical vinyl polymerization*, the electrons in the pi bond split up. One combines with the unpaired electron in the initiator (or growing chain end) to form the new bond, and the second ends up on the chain end, reproducing the attacking species.

In *anionic vinyl polymerization*, the electrons in the pi bond move together instead of separately. The initiator (or growing chain end) attacks with a pair of electrons, used to form the new bond. The pi-bond electron pair "flows" away from the attacking species, reproducing the anion at the chain end.



Cationic vinyl polymerization is exactly the same mechanism, except that the initiator (or chain end) lacks a pair of electrons. The electron "flow" is simply in the opposite direction, leaving behind a positive charge at the chain end to continue the process.



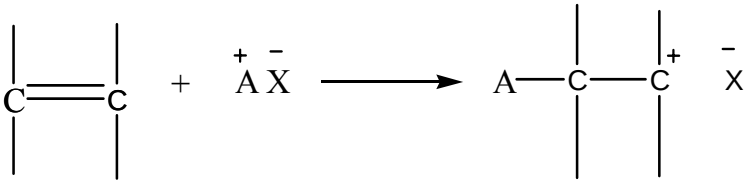
One important difference: ionic polymerizations necessarily carries along a counter ion, and their rates are much more sensitive to reaction conditions (e.g., solvent polarity, and temperature).

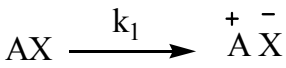
Cationic polymerization

Cationic polymerization is induced by initiators that release cations in the reaction mass. The classes of common initiators are:

1. Protonic acids- HCl, H_2SO_4, Cl_3CCOOH, $HClO_4$
2. Aprotic acids- BF_3, $AlCl_3$, $TiCl_4$, $SnBr_4$
3. Carbonium salts- $AlEt_3$, $AlEtCl_2$
4. Cationogenic substances- t-$BuClO_4$

Initiation

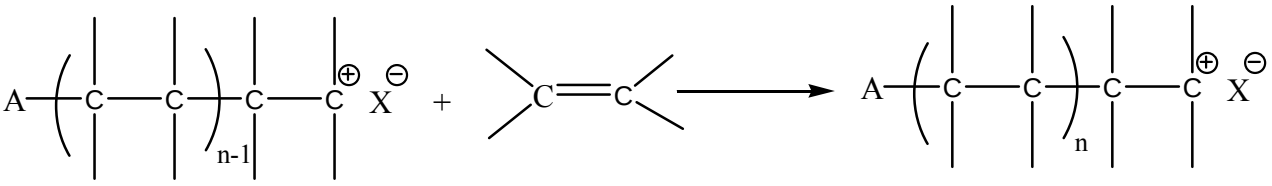




k_1 = initiation rate constant

$$r_i = k_1 [AX]$$

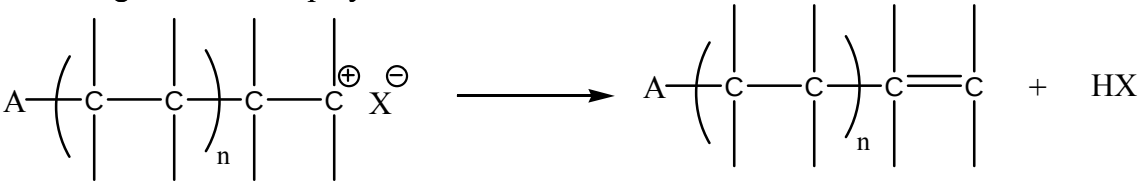
Propagation



A positive charge of the polymer ions is transferred to other molecules in the reaction mass. These could be impurity molecules or monomer molecules themselves.

Termination

No mutual termination occurs in cationic polymerization because of the repulsion between the like charges on the two polymer chains



Anionic polymerization

Anionic polymerization is initiated by compounds that release anions in the reaction mass. The process, also known as the Ziegler Natta process, is used to produce most of the high density polyethylene and polypropylene made worldwide. However, due to the sensitivity of the Ziegler/Natta process to impurities such as water and its intolerance to many functional groups the process has been limited only to the select polymers such as high density polyethylene and polypropylene.

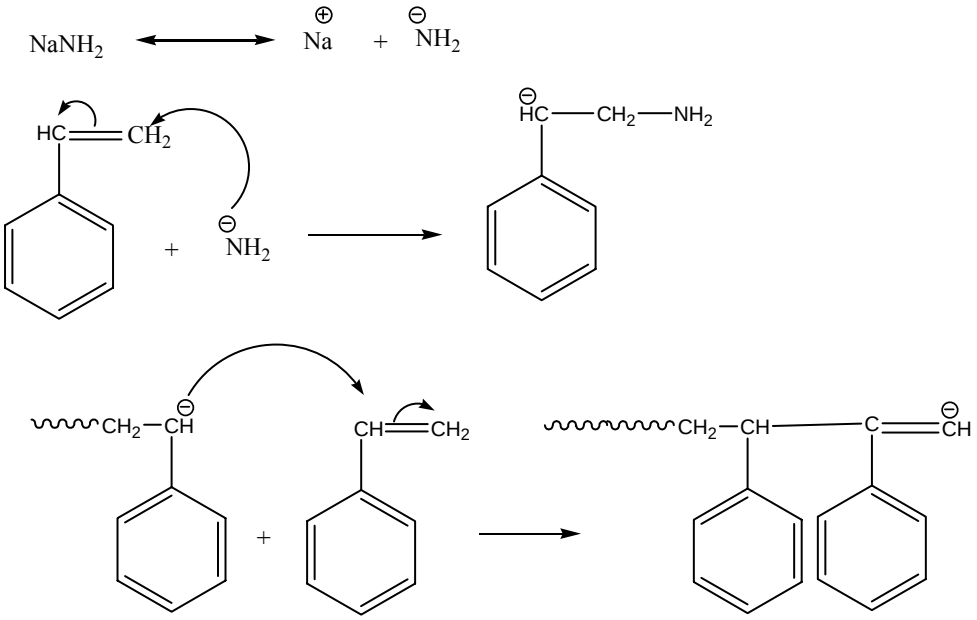
Anionic polymerization consists essentially of only two elementary reactions:

- ❖ Initiation
- ❖ Propagation

The transfer and termination reactions do not occur, especially where the impurities to which the catalysts are sensitive are absent.

Initiators for anionic polymerization:

1. Alkali metals and alkali metal complexes (Na, K, Li and their stable complexes)
2. Organometallic compounds (butyl lithium)
3. Lewis base (ammonia, triphenyl methane, xanthene, aniline)
4. High energy radiation (γ radiation, e^- beam)



Condensation Polymerization

Monomer molecules consisting of atleast two functional groups can undergo condensation polymerisation or step-growth polymerization. Condensation polymerization occurs when monomers bond together through covalent and water is "condensed" out during the reaction.

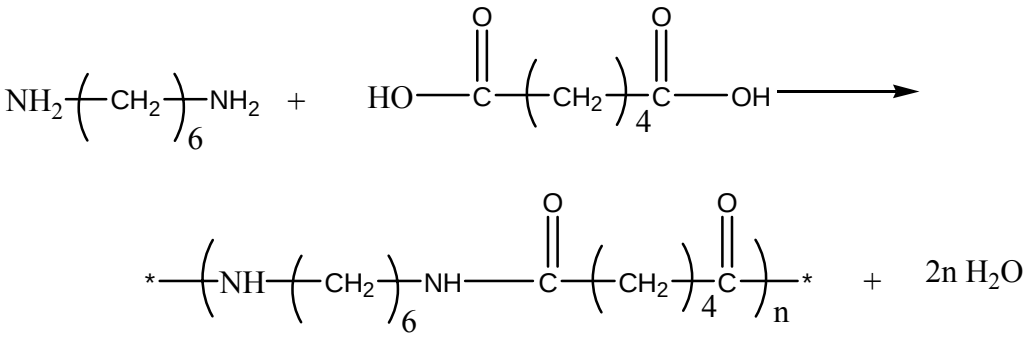
Since the p[olymerisation proceeds with the evolution of water molecule each time the condensation takes place, presence of a carboxylic acid group and hydroxyl or amino groups, is essential.

The polymerisation, thus, takes place when :

(a) Both the reacting functional groups are present in the same monomer.e.g. aminocaproic a

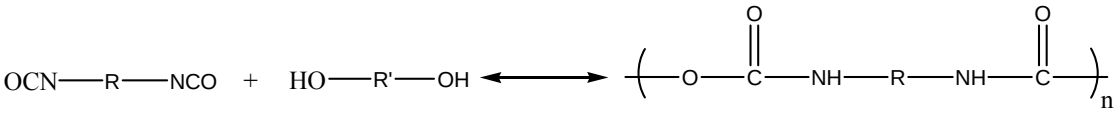
H_2N-----$(CH_2)_5$------COOH . Here, the monomer molecules condense by the reaction between carboxylic group from one molecule and amino group from the other and in this way, polymerisation proceeds.

(b) Two different monomers one having the two hydroxyl groups such as ethylene glycol and the other one with two carboxylic acid groups such as terephthalic acid to produce polyesters. Similarily, the condensation of hexamethylene diamine and adipic acid leading to Nylon 6,6.



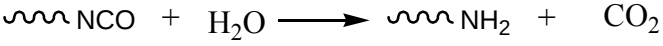
When an amine reacts with a carboxylic acid, an amide or a peptide bond is formed, with the release of water (hence *condensation* polymerization.) This is the process through which amino acids link to form proteins, as well as how Kevlar, a polyamide and trademark of Dupont is formed.

Step growth polymers are defined as polymers formed by the stepwise reaction between functional groups of monomer. Not all step growth polymers (like polyurethanes formed from isocyanate and alcohol bifunctional monomers) release condensates. Polyurethanes are a class of condensation polymers formed by the step growth polymerization of a diol and a di-isocyanate as follows

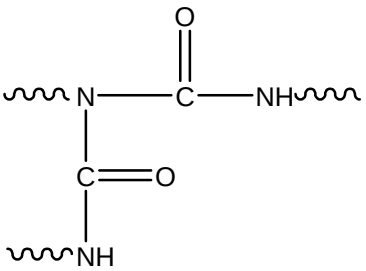


The di-isocyanates used are either 2, 4-toluene di-isocyanate (TDI) or 4, 4'-diphenyl methane di-isocyanate (MDI).

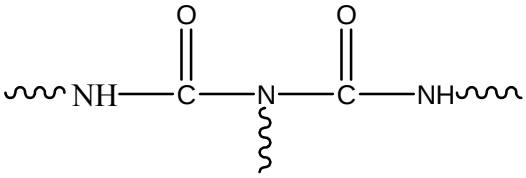
The isocyanate group reacts with water to release carbon-dioxide.



The carbon dioxide thus liberated initially leaves the reaction mass, but with the progress of polymerization, the viscosity increases and the gas is trapped, giving a cellular structure. The urethane formed is not necessarily linear, but branches are generated through allophanate linkage and biuret linkage.



Allophanate linkage



Biuret linkage

Step growth polymers increase in molecular weight at a very slow rate at lower conversions and only reach moderately high molecular weights at very high conversion (i.e. >95%).

Hydrated Silicates

The essential ingredients of concrete are cement, water, and aggregate. When all are mixed together, the silicate polymers start to form. As water evaporates, the polymers can get quite large and can bind together and enclose the aggregate (gravel and sand) together. It is a process that starts by hydrating the silicates and continues by condensation and removal of condensed water out of the structure.

Polyesters and polyamides are the two important classes of condensation polymers.

Polyesters

Polyesters contain ester linkages in their main chain. The well known polyester is made by reacting benzene-1, 4-dicarboxylic acid and ethane-1, 2-diol, and is well known commercially by the names Dacron and Terylene **(FigXXX).** The properties of the polyesters are determined by the properties of carboxylate ester groups in the structure, geometry, polarity and segmental mobility of the repeating units. Since their intermolecular interactions are not especially strong, the properties of polyesters are more sensitive to variations in structure.

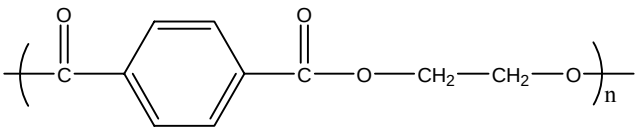


Fig XXX: Polyester made by reacting benzene 1,4-dicarbazole acid and ethane 1,2-diol.

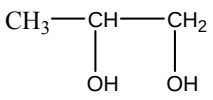
The ester link in the molecule affects the properties of the molecules in the following ways:

1. The ester group is a point of weakness, being susceptible to hydrolysis, ammonolysis and ester interchange, the first two reactions leading to chain scission. The reactivity is influenced by the nature of the adjacent groupings.

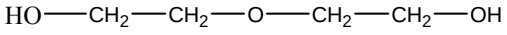
2. The ester group is a highly polar group and can affect high frequency electrical insulation properties. The polar ester group acts as a proton acceptor, allowing interactions of inter or intra molecular nature.
3. The ester group enhances chain flexibility of the polymethylenic chain.

Raw materials for the synthesis of polyesters include :

1. **Glycols**- 1,2 propylene glycol (diethylene and triethylene glycol) are used to obtain products with greater water absorption and inferior electrical properties.
2. **Acids**- Phthalic anhydride, Terephthlic acid and adipic acid are the acids used in the preparation of esters.



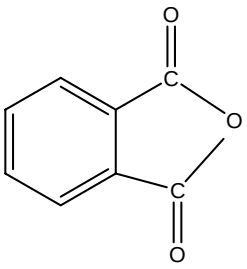
1, 2- propylene glycol



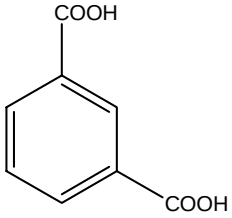
Diethylene glycol

3. **Acids**- Phthalic anhydride, Terephthlic acid and adipic acid are the acids used in the preparation of esters.

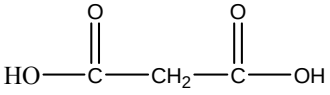
Phthalic anhydride is used for rigid resins, it provides rigidity to the structure. Isophthalic acids and adipic acid are used for the preparation of resistant gel coatings.



Phthalic anhydride



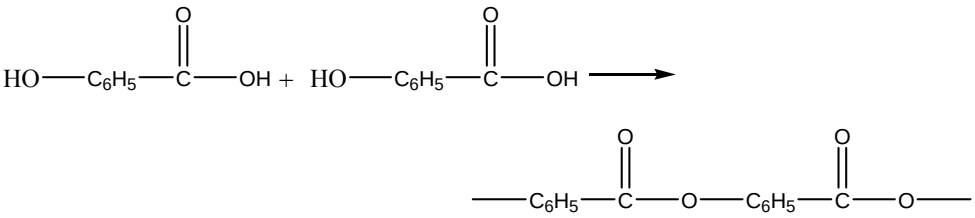
Isophthalic acid



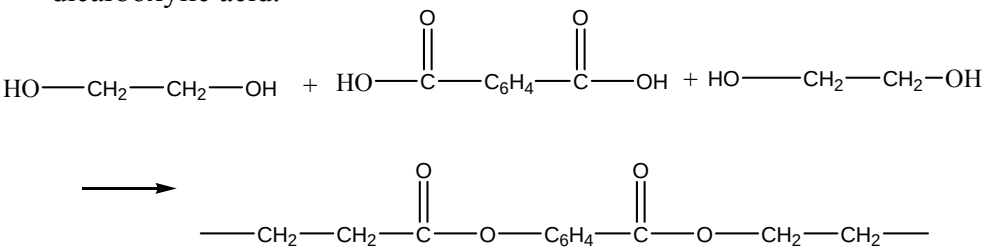
Adipic acid

The starting reactants for the manufacture of the wide range of polyesters are products of downstream petrochemical operations. Polyesters may be produced through following techniques.

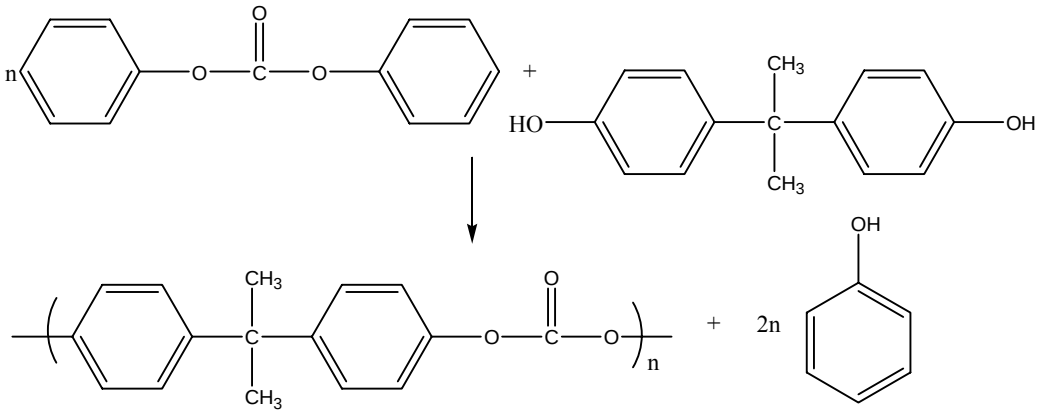
1. Self-condensation of ω-hydoxy acids



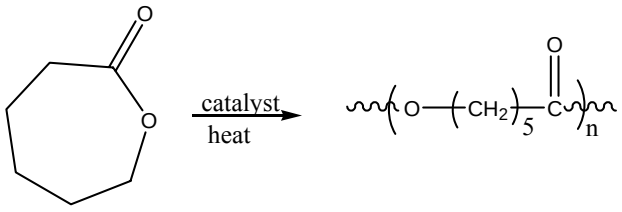
2. Condensation of polyhydroxy compounds with polybasic acids, example: a glycol with a dicarboxylic acid.



3. Ester exchange



4. Ring opening of caprolactone with dihydroxy or trihydroxy initiators.



ξ Caprolactone

Poly(ξ Caprolactone)

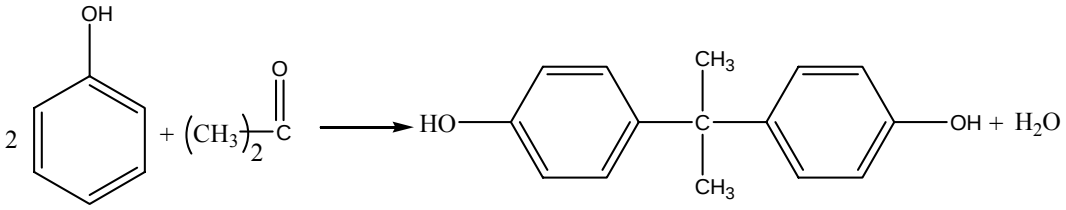
Applications

1. Laminating resins
2. Molding composition
3. Fibers and films
4. Surface coating resins
5. Rubbers and plasticizers

Polycarbonates

Polycarbonates belong to the group of polyesters. Polyhydroxy compounds react with a carbonic acid derivative, a series of polymers are produced with carbonate (- O - CO – O) linkages. Such polymers are called polycarbonates.

For example: Bis- phenol A is produced by the condensation of phenol with acetone under acidic conditions.

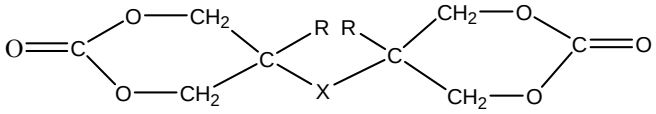


The initial product is iso-propenyl phenyl which reacts with a further molecule to form bis-phenol A. in order to achieve a high yield, an excess of phenol is used and the initial reaction product is a bis-phenol A phenol adduct.

Polycarbonates are classified into:

1. Aliphatic polycarbonates
2. Aromatic polycarbonates

Ring opening polymerization of six-membered cyclic carbonates (1,3-dioxan-2-one) in the presence of bicyclic carbonates act as cross-linking agents, leading to hard, tough thermosets.



Cross-linked polycarbonates with outstanding properties are obtained by free radical polymerization of diethylene glycol bis allyl carbonate.

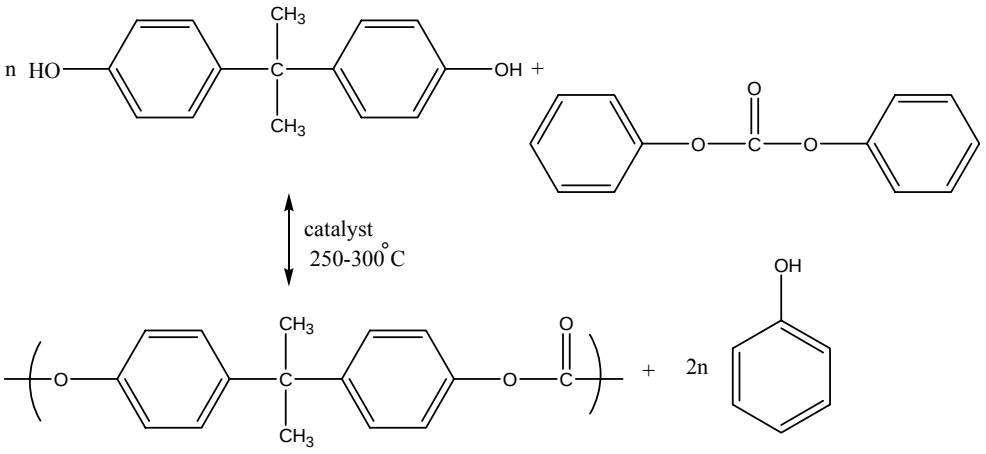
Properties : Linear aliphatic polycarbonates with molecular weights upto 30, 000 are obtained by transesterification while those with a molecular weight > 50, 000 are prepared by polymerization of carbonates possessing six-membered rings.

Aromatic polycarbonates are prepared by the reaction of bis-phenols with cabonic acid derivatives. Aromatic diesters of carbonic acid are condensed with dihydroxy diaryls in the presence of basic catalysts to give high molecular weight polycarbonates.

Bisphenol A polycarbonates are insoluble in water, alcohols, organic acids.

Applications

a) Electrical applications
b) Household and consumable articles
c) Automotive applications

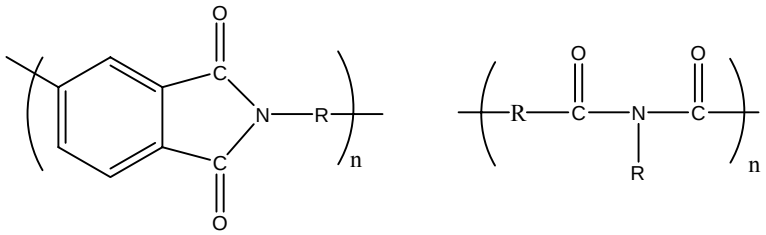


Polymides

Polymides can be either polyimides and polyamides. Let us discuss them one by one.

Polyimides

Polyimides are condensation polymers derived from bifunctional carboxylic acid anhydrides and primary diamines. They contain the imide structure –CO-NR-CO- as a linear or heterocyclic unit along the main chain of the polymer backbone.



So, if the molecule shown was to be polymerized the product would be a polyimide **(Fig XXXI).**

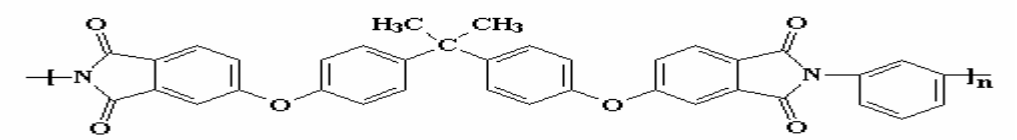
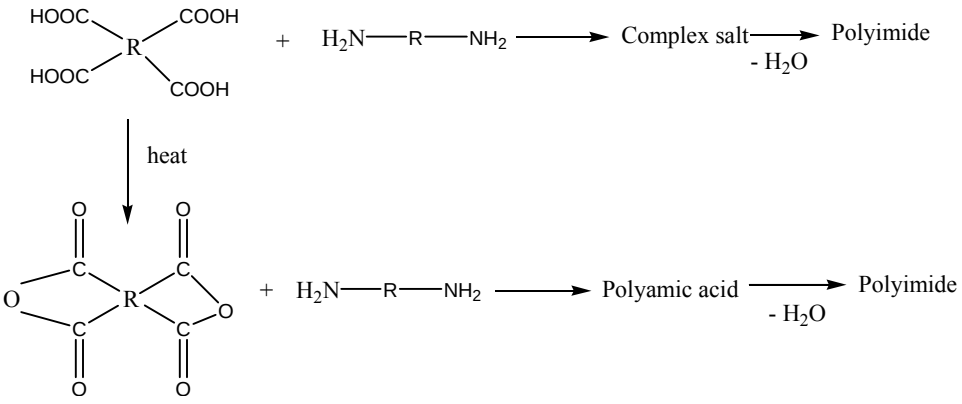


Fig XXXI: Polymer consisting of an imide linkage. Polyimides are used in various day to day applications like circuit boards, microwave cookware, etc.

Raw materials

Polyimides are prepared by the condensation of aromatic or aliphatic tetracarboxylic acids or anhydrides with primary aromatic or aliphatic diamines.



Complex oligomeric amine salts are formed initially. Heating these salts in solution or in the melt at 150-300^0 C results in the loss of water and formation of polymer.

Polyimides are considered specialty plastics because of their outstanding high performance engineering properties. These materials are widely used in place of metals and glass in high performance applications such as aerospace and automotive industry.

Polyimides are a very interesting group of incredibly strong and astoundingly heat and chemical resistant polymers. Their mechanical strength, heat and chemical resistance is so great that these materials often replace glass and metals, such as steel, in many demanding industrial applications. Polyimides are also used in many everyday applications. They are used for the struts and chassis in some cars as well as some parts under-the-hood because they can withstand the intense heat and corrosive lubricants, fuels, and coolant that cars require. They are also used in the construction of many appliances as well as microwave cookware and food packaging because of their thermal stability, resistance to oils, greases, and fats and their transparency to microwave radiation. They can also be used in circuit boards, insulation, and fibers for protective clothing, composites, and adhesives.

Another interesting property of polyimides, which makes them excellent for use in construction and transportation industries, is that they burn.
When an aromatic polyimide catches fire, which by the way is difficult to begin with, a surface char develops which smothers the flame, blocking it from the fuel to burn.

Polyamides

Polyamides are polymers where the repeating units are held together by amide links. An amide group has the formula –$CONH_2$. An amide link has the structure as in **Fig XXXII.** Polyamides are formed by the piolymerisation of a diamine and a dicarboxylic acid and are commonly known as Nylons.

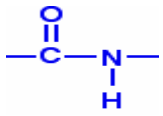
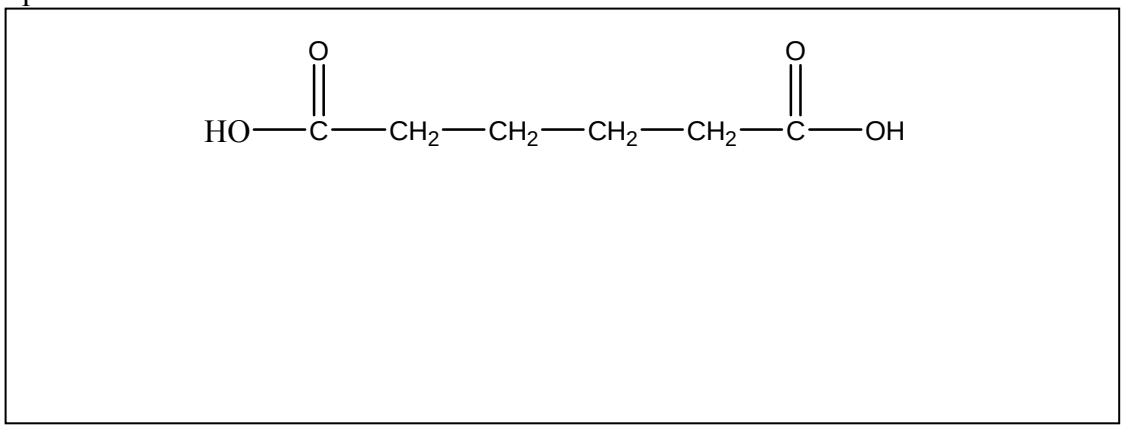


Fig XXXII: General structure of an amide link.

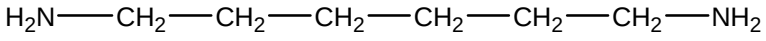
Nylon

In nylon, the repeating unit contains chains of carbon atoms. There are various different types of nylon depending on the nature of those chains. Nylon 6,6 and Nylon-6 are the commercially important polyamides among the various Nylons.

Nylon 6,6: It is made from two monomers each of which contains 6 carbon acid with a –COOH group at each end –hexanedioic acid.



The other monomer is a 6-carbon chain with an amino group at each end. This is 1,6-diaminohexane



When these two compounds polymerize, the amine and acid groups combine, each time with the loss of a water molecule to yield Nylon 6,6.

Nylon-6: Nylon-6 is made from a monomer called caprolactum. This molecule already contains an amide link which polymerizes to give the structure as in **Fig XXXIII**

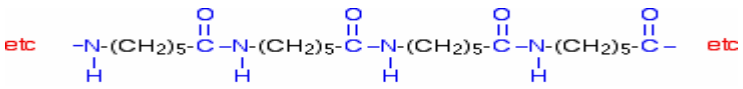


Fig XXXIII: Depiction of a polyamide (Nylon 6) formed by using caprolactum as a monomer.

Phenol Formaldehyde Resin

Phenol formaldehyde resins are an important class of condensation polymers known as phenolic resins commonly known as PF resins.

Phenolics are resinous materials produced by the condensation of phenol with formaldehyde.

(1) Phenol formaldehyde resins, as a group, are formed by a step-growth polymerization reaction which may be either acid or base catalysed. The pathway the reaction follows varies depending on the catalyst used.

(2) Phenol formaldehyde resins, as a group, are formed by a step-growth polymerization reaction which may be either acid or base catalysed. The pathway the reaction follows varies depending on the catalyst used. When polymerised at acidic pH , Novolac is formed. Under basic conditions, a highly branched polymer called resole is formed.

Phenol is reactive towards formaldehyde at the *ortho* and *para* sites (sites 2, 4 and 6) allowing upto 3 units of formaldehyde to attach to the ring. This forms a hydroxymethyl phenol, which is not usually isolated in novolacs but is found in resoles (see below). The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction forms a methylene bridge, and the second forms an ether bridge.

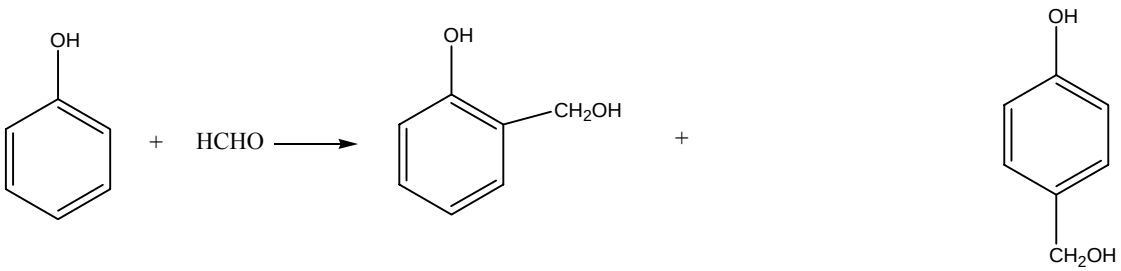
Phenol formaldehyde resins, as a group, are formed by a step-growth polymerization reaction which may be either acid or base catalysed. The pathway the reaction follows varies depending on the catalyst used.

Phenols and cresols are the most widely used phenols, whilst formaldehyde and furfural are the widely used alsdehydes for the manufacture of phenolic resins.

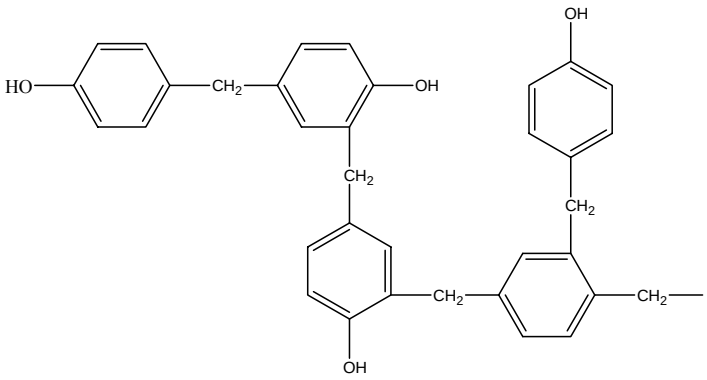
Reaction of phenol with formaldehyde involves a condensation reaction, which leads, under appropriate conditions to a cross-linked polymer structure. Phenol reacts with formaldehyde to produce two types of resins-novalaks and resols.

Novalaks

Novalaks are prepared by reacting phenol with formaldehyde in a molar ratio of 1:0.8 under acidic conditions. Under these conditions, a slow reaction takes place to form o- and p-hydroxyl methyl phenols.



When novalak resins are mixed with compounds capable of forming methylene bridges such as hexamethylene tetramine/ paraformaldehyde, they cross-link on heating to form infusible, thermoset structures.



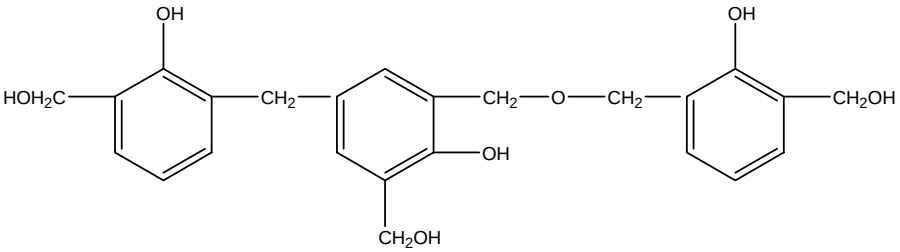
The novalaks are referred to as two stage resins, since the formation of a cross-linked resin involves two steps. The first stage involves the methylol groups and the second stage involves the cross-linking by the addition of a cross-linking agent. Novalaks and resols are soluble and fusible low molecular weight products.

Acid catalysed phenol formaldehyde resins are made with a molar ratio of formaldehyde to phenol of less than one and are called novolacs. Owing to the molar ratio of formaldehyde to phenol, they will not completely crosslink (polymerize) without the addition of a crosslinking agent. Novolacs are commonly used as photoresists.

Resols

Resols are formed by the reaction of phenol with an excess of formaldehyde under basic conditions. The formation of phenol-alcohol is rapid but their subsequent condensation is slow. There is a tendency for polyalcohols as well as monoalcohols to be formed.

Liquid resols will have an average of less than two benzene rings per molecule while a solid resol may have only three to four. Heating of these resins will result in cross-linking via the uncondensed methylol groups.



The curing of resols does not require any additional curing agent. It is heat cured at $150^0 - 200^0$c and the network polymer is called resite.

Resols are known as one stage resins due to the fact that a cross-linked resin can be obtained in the initial stage itself.

Base catalyzed phenol formaldehyde resins are made with a molar ratio of formaldehyde to phenol ratio of greater than one (usually around 1.5). Phenol, formaldehyde, water and catalyst are mixed in the desired amount, depending on the resin to be formed, and are then heated. The

first part of the reaction, at around 70 °C, forms hydroxymethyl phenols. This results in a thick reddish-brown goo, the resin.

The rate of the base catalysed reaction initially increases with pH, and reaches a maximum at approx. pH = 10. The reactive species is the phenolic anion formed by deprotonation of phenol. The negative charge is delocalised over the aromatic ring, activating sites 2, 4 and 6, which then react with the formaldehyde.

Formaldehyde in solution does not exist as the aldhehyde, but instead a dynamic equilibrium is formed creating a range of methylene glycol oligomers, and the concentration of the *reactive* form of formaldehyde depends on the exact conditions (temperature, pH) under which the reaction occurs. Thus the reaction rate law describing phenol and formaldehyde is not a simple one, and the chemical kinetics are highly complex.

Hydroxymethyl phenols will crosslink on heating to around 120 °C to form methylene and methyl ether bridges. At this point the resin is starting to crosslink, to form the highly extended 3-dimensional web of covalent bonds which is typical of polymerised phenolic resins. It is this highly crosslinked nature of phenolics which gives them their hardness and their excellent thermal stability and which makes them impervious to most chemical attack and solvation. It is also the reason they are called thermosets.

Crosslinking and the phenol/formaldehyde ratio

Phenol can react with formaldehyde at any one of three possible sites, and formaldehyde can react with up to two molecules phenols. Thus the theoretical functionality of phenol is three and the theoretical functionality of formaldehyde is two. The actual functionality that is found in the polymer depends on the phenol:formaldehyde ratio.

To phenol, acid catalyst such as p-toluenesulfonic acid is added to which formaldehyde is added slowly. Under these conditions, formaldehyde will react between two phenols to form a methylene bridge, creating a dimer. As more formaldehyde is added, more molecules of phenols will be crosslinked together, generating more dimers . As the concentration of dimers increases, there is the possibility of generating trimers, tetramers and higher oligomers.. This is what occurs during the formation of a novolac. The average molecule generated depends on the ratio of formaldehyde to phenol. In novolacs this is usually around 0.8, and so, with 5 phenols for every 4 formaldehyde molecule the *average* molecule is a pentamer .

With equimolar ratios of formaldehyde and phenol, a completely crosslinked structure is formed. Phenolic resins have high voltage insulation applications, good rigidity, good strength and machinability.

Applications

1. Phenolic resins are used in surface coating of materials

1. High voltage insulation applications
2. Phenolic resins are used in surface coating of materials
3. Resols are useful for storing laquers for coating chemical plant, textile equipment, razor blades, brassware and food cans

4. Phenolic aresins are used with poly vinyl acetate as a flexible, tough and solvent resistant wire strand.
5. Resols are used for plywood glues having good resistance to aging.

Urea Formaldehyde Resin

Urea formaldehyde resins belong to a group of plastics known as aminoplastics. Aminoplastics are co-condensates of urea, melamine and formaldehyde. Of the various amino resins, urea formaldehyde resins are the most important. Urea formaldehyde resins are formed by the reaction between urea and formaldehyde, resulting in the formation of a cross-linked, insoluble, infusible material. The reaction involves condensation between the nucleophilic nitrogen of urea with the electrophilic carbonyl carbon of formaldehyde. A branched copolymer is formed **Fig XXXIV**.

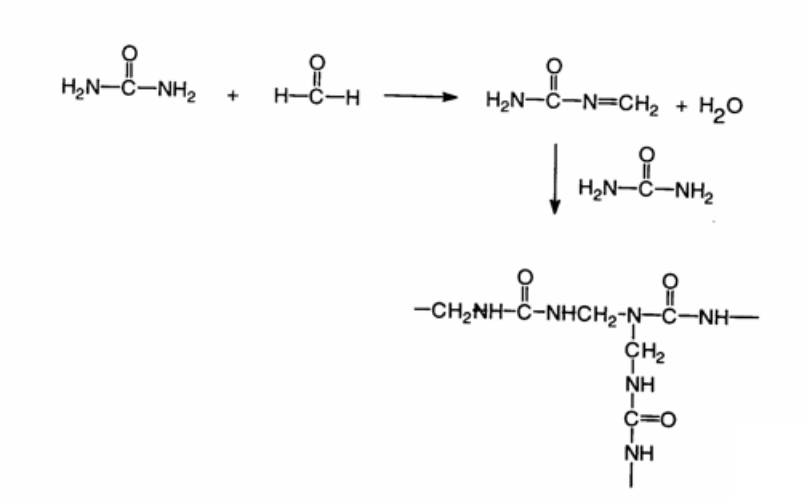


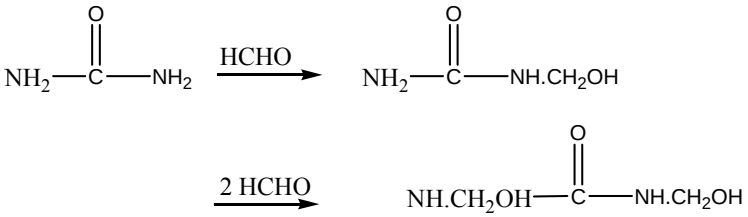
Fig XXXIV: Reaction of urea and formaldehyde to yield urea-formaldehyde resin product.

Urea formaldehyde resins are used chiefly in the manufacture of buttons, baking enamels, and for making fabrics wrinkle-resistant.

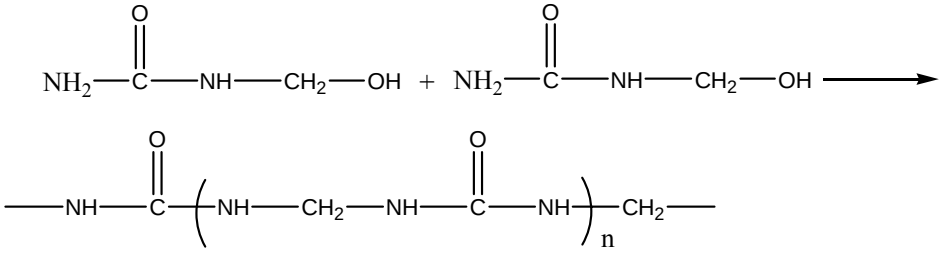
Methods of preparation:

Urea formaldehyde resins are prepared by a 2-stage reaction

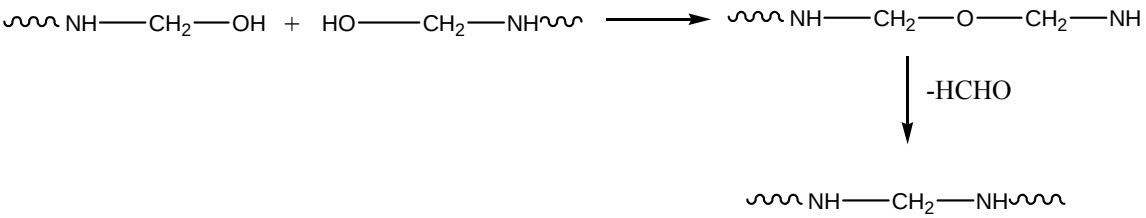
First stage: Urea reacts with formaldehyde under neutral or mildly alkaline conditions, leading to the production of dimethylol urea.



This stage may consist of unreacted urea and formaldehyde which when heated under acidic conditions at elevated temperatures leads to the formation of a hard, colorless, transparent and infusible mass is formed (gel).
The methylol urea condenses with each other by reaction of a CH_2OH of one molecule with an NH_2 group of another molecule.



The methylol groups formed at the end of the chain can react with other methylol groups to give ether linkages or with amine groups to give methylene linkages. The ether linkages break down to methylene linkages on heating with the evolution of HCHO.



Properties and applications

1. Low cost materials
2. They do not impart taste and odor to foodstuffs or beverages with which they come in contact
3. Good electrical insulation
4. Heat resistance up to 70°C

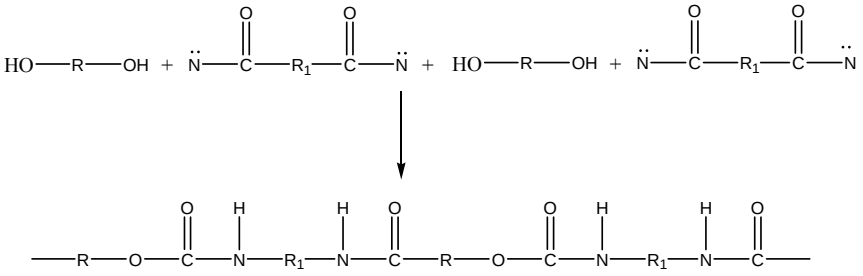
The limited heat resistance, water resistance and stain resistance limits the suitability of urea formaldehyde resins for domestic appliances.

a) Toilet seats and miscellaneous bathroom equipments
b) Hair dryer, vacuum flask jugs and cups
c) Knobs, switches and lampshades
d) Adhesives for particle board and furniture industries
e) Foams and firefighters
f) Textile finishing agents
g) Meal trays and toys

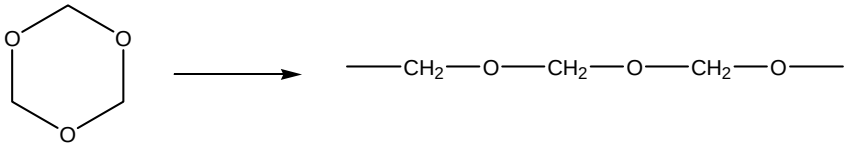
---- are used as plasticizers in rubbers but they cross-link during vulcanization to give a hard product with improved oxidation resistance, oil resistance and tensile strength.

Rearrangement Polymerization

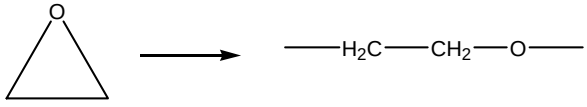
It is a type of polymerization which is intermediate between addition and condensation polymerization. No molecule is split out and the reaction kinetics is similar to that of condensation polymerization. Preparation of polyurethanes by the reaction of diols with diisocyanate is the best example of rearrangement polymerization.



One variation of rearrangement polymerization is **ring-opening polymerization**. Important examples include the polymerization of trioxane, ethylene oxide.



Trioxane



Ethylene oxide

Epoxy resins

Epoxy resins are a class of resins produced by the polymerization of epichlorohydrin with diphenylolpropane **Fig XXXV.**

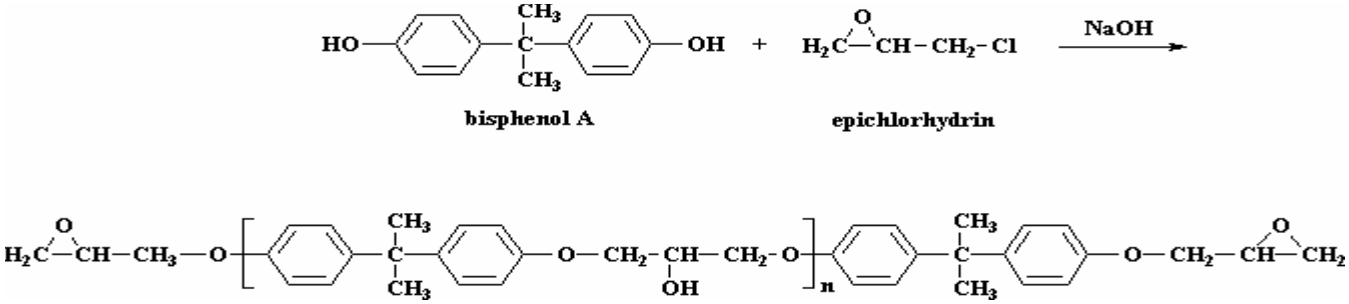
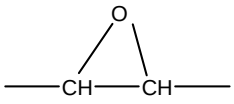


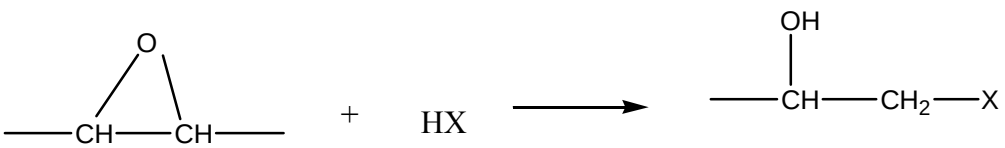
Fig XXXV: Polymerization of epichlorohydrin and bis phenol-A under alkaline conditions leading to an epoxy resin.

A range of resins of widely differing molecular weights, e.g., 400 to 6,000, can be produced by varying the proportion of reactants, as well as reaction conditions. These materials are noted for their versatility, but their high cost has limited their use. High resistance to chemicals and outstanding adhesion, durability, and toughness has made them valuable as coatings. Because of their high electrical resistance, durability at high and low temperatures, and the ease with which they can be poured or cast without forming bubbles, epoxy resin plastics are especially useful for encapsulating electrical and electronic components. Epoxy resin adhesives can be used on metals, construction materials, and most other synthetic resins. They are strong enough to be used in place of rivets and welds in certain industrial applications.

Epoxy resins are characterized by the presence of one or more epoxy groups per molecule.

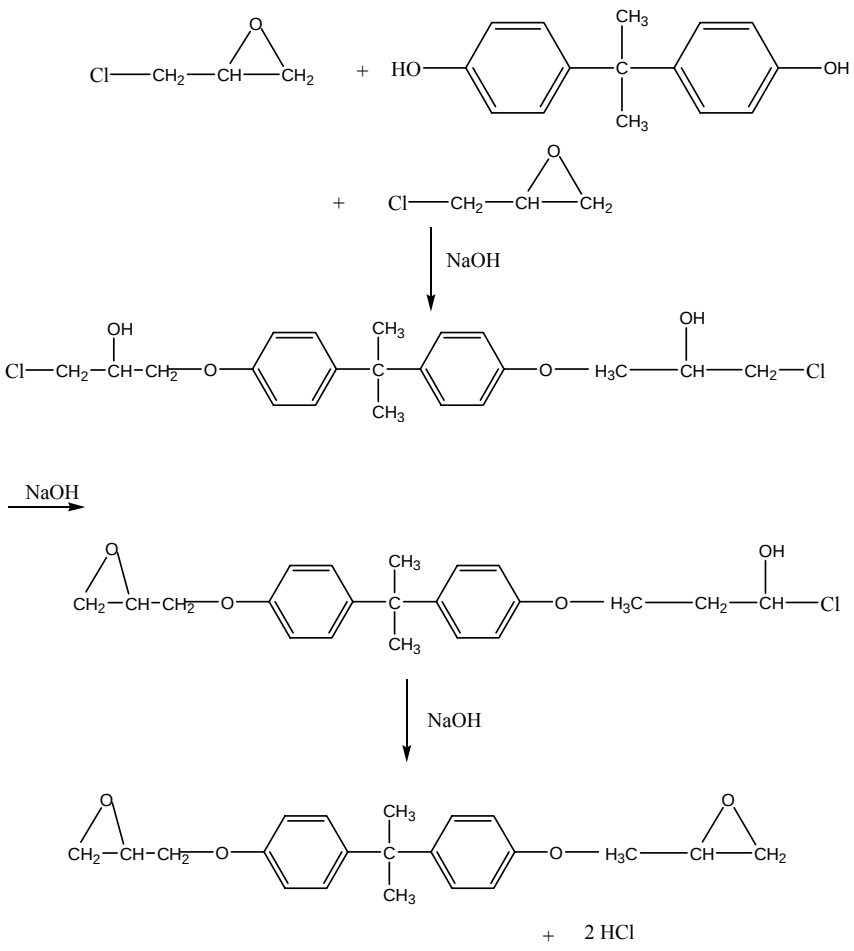


The three membered epoxy ring is highly strained and is therefore reactive to many substances

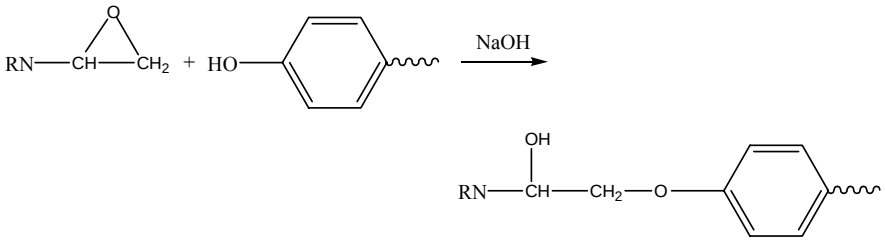


Such reactions allow chain extension and cross-linking to occur without the elimination of water or small molecules; they react by a rearrangement polymerization type of reaction. The non-epoxy part may be aliphatic, aromatic or cycloaliphatic.

Preparation of epoxy resins: The most important commercial epoxide resins are reaction products of bis phenol A and epichlorohydrin.



The general formulae:



When n=0, the product is diglycidyl ether and the molecular weight is 340; when n=10, molecular weight is 3000; commercial resins having a molecular weight exceeding 4000, the epoxy resins are polymers with a low degree of polymerization.

Polyurethanes

Polyurethanes are an important family of synthetic organic polymers obtained by the reaction of bi-functional isocyanates with bi-functional alcohol. One obtains linear macromolecules that are characterized by the regular repetition of the urethane groups. The presence of the urethane group permits the build up of a three dimensional network because of the reaction of the hydrogen of the –NH- group with the terminal isocyanate (-NCO) group of the chain. These networks are either elastomeric or rigid; they are used with great success in the field of elastomeric fibers and in making both soft and rigid foams.

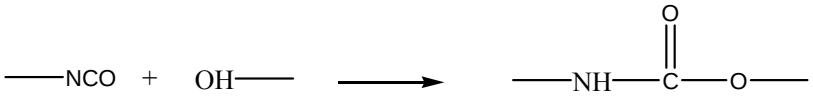
Three major types of polyurethanes are:

1. One type is based on ether or ester type pre-polymers that are chain extended and cross linked using polyhydroxyl compounds of amines; unsaturated groups may be introduced to permit vulcanization with common curing agents such as peroxides.

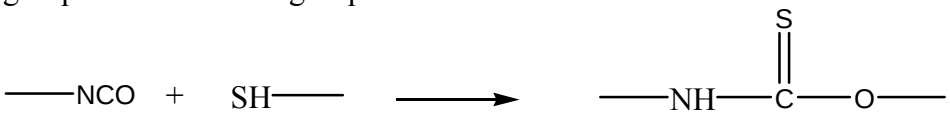
2. A second type is obtained by first casting a mixture of pre-polymer with chain extenders and cross linking agents, and then cross linking further by heating.

3. The third type is prepared by reacting a di-hydroxy ester or ether type pre-polymer with a diisocyanate and a diol; these thermoplastic elastomers can be processed on conventional plastic equipment.

Polyurethanes are prepared by the addition polymerization where two or polyfuctional hydroxyl or amine group containing compounds is reacted with di or polyisocyanates. The characteristic structural element of all these polymers is the urethane group formed in the course of the addition.

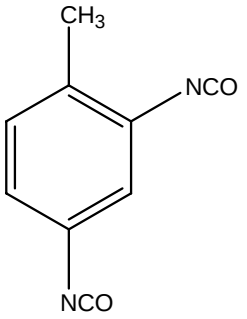


Thiourethanes is another important class of urethane polymers formed by the reaction of the –SH group with the –NCO group.

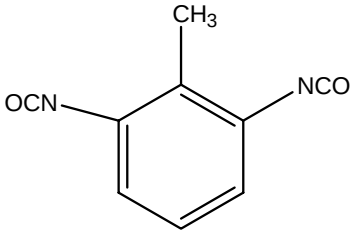


Raw materials

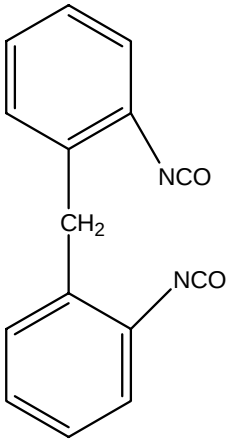
Isocyanates-aromatic, aliphatic and cycloaliphatic di- or poly-isocyanates are suitable building blocks for polyurethane chemistry. Toluene diisocyanate (TDI) and methylene diisocyanate (MDI). Are examples of aromatic isocyanates used in the urethane chemistry.



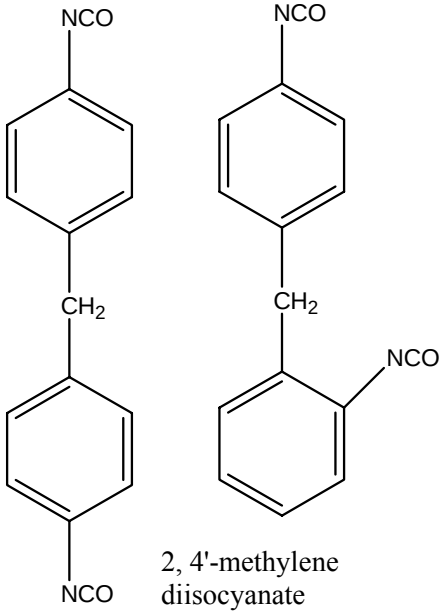
2, 4-toluene diisocyanate



2, 6-toluene diisocyanate



2, 2'-toluene diisocyanate



2, 4'-methylene diisocyanate

4, 4'-methylene diisocyanate

Rubbers and Elastomers – Natural and Synthetic Rubbers

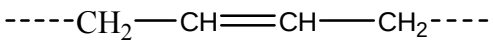
Rubber is a polymer with elastic properties. It occurs as a milky emulsion (known as *latex*) in the sap of several varieties of plants. Rubber can also be produced synthetically. Synthetic rubber is made by the polymerization of a variety of monomers .

Natural and synthetic rubbers are materials whose glass transition temperatures Tg are lower than the temperature of application. Rubber can be stretched upto 700 % and exhibit an increase in modulus with temperature.

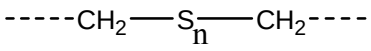
Natural Rubber

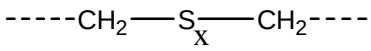
Properties: Hevea latex , collected from the bark of Hevea Brasiliensis, has close to 33% dry rubber content. Natural rubber or natural latex is nothing but the dispersion of polymeric material in water as an emulsion. It is a long chain of polyisoprene and is prepared by breaking the emulsion which means by coagulating the latex with acetic acid as the coagulating agent. The latex from different plants are known to have are known to have varying contents of dry rubber, for example , Hevea latex , collected from the bark of Hevea Brasiliensis, has close to 33% dry rubber content and is used in adhesives, gloves, contraceptives, latex foam and medical tubing.

Natural rubber has the property of natural tack and therefore it serves as an excellent adhesive. Adhesion occurs because the ends of rubber molecules penetrate the adherend surface and then crystallise. The polymer has the following chemical structure, having a double bond at every alternate carbon atom.



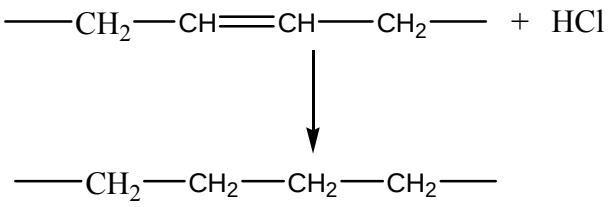
Rubber can react with sulfur to form a polymer network having sulfur bridges as follows:





This process of formation of S linkages is known as vulcanization. The vulcanized rubber is tough and is used in manufacture of tires. As the sulfur content increases, the vulcanized rubber loses its elasticity or rubbery nature. Generally, the sulfur content is kept at 2-3 %.
When sulfur content is increased to 30 %, the resultant material is a very hard non - rubbery material known as “ebonite” or hard rubber.

Similarly, treatment of natural rubber with chlorine gives chlorinated rubber, which has the following structure. The double bonds of natural rubber can easily undergo addition reactions with hydrochloric acid, forming rubber hydrochloride. Chlorinated rubber is extensively employed in industry for corrosion resistant coatings.



In its relaxed state, rubber consists of long, coiled-up monomer chains that are interlinked at a few points. Between a pair of links each monomer can rotate freely about its neighbor, to assume a large number of geometries, like a very loose rope attached to a pair of fixed points. At room temperature, rubber stores enough kinetic energy so that each section of the chain oscillates chaotically, like a piece of rope being shaken violently. When rubber is stretched, its behavior akin to the "loose pieces of rope" is restricted, as the polymer chains are not able to oscillate. Their kinetic energy is given off as excess heat. In going from the relaxed to the stretched state, the entropy decreases and it increases during relaxation. This change in entropy can also be explained by the fact that a tight section of chain can fold in fewer ways than a loose section of chain, at a given temperature. Relaxation of a stretched rubber band is thus, driven by an increase in entropy, and it is a result of the thermal energy of the material being converted to kinetic energy. Rubber relaxation is endothermic as it undergoes adiabatic cooling during contraction. This can easily be sensed by holding a stretched rubber onto your lips and then slowly relaxing it.

Stretching of a rubber band is in some ways equivalent to the compression of an ideal gas, manifested as rise in temperature and relaxation as equivalent to the expansion of gas resulting in cooling effect. Moreover, the compression and expansion of a gas is like the elastic behavior of rubber, for example, an inflated car tyre.

Likewise, stretching of rubber reduces the "space" available to each section of polymer chain as it is evident in the case of compression of a gas caused by reduction in volume of the gas.

Vulcanization of rubber creates disulphide bonds between the chains making the free section of the polymer chain shorter. As a result, the polymer chains tighten more quickly for a given length of strain and rubber becomes harder as well as less extendable.

When cooled below its glass transition temperature, the flexible chain segments "freeze" into fixed geometries and the rubber loses its elastic properties, though this process is reversible. At very cold temperatures rubber becomes brittle and it will break into shards when struck. It is because of this reason that the tyres are made up of the softer version of rubber so that tyre can withstand the low temperatures during winters.

Current sources of rubber

Today, Asia is the main source of natural rubber. Over half the rubber used today is synthetic, but several million tones of natural rubber are still produced annually, and is still a preferred raw material for applications such as automotive and some military equipment.

Natural rubber is often vulcanized by heating it with sulfur or sulfur derivatives. Carbon black is often used as an additive in the vulcanized rubber to produced the tyres with improved strength.

Environmental Effects: Oxygen and particularly ozone cause surface cracking when even a low threshold value of tensile stress is applied. Depending upon the external stress pattern, actual penetration of the oxygen and ozone can be low, with the inside being protected by the degraded exterior.

Mechanical Effects: In tension, ozone cracking can propagate quite rapidly through an otherwise satisfactory sample; the lives and performance of thin and thick items made of the same material in the same environment can be very different. Articles in shear or compression remain unaffected provided that the surface itself does not enter a tension mode but this can be ensured only by design.

Oils and Solvents: Both oils and solvents can cause a loss of physical strength; with thin articles being the worst affected. Attack by contact with oils and solvents depend on the thickness of surface layer and the diffusion rate of oil and solvents. Lighter solvents will attack the rubber more rapidly, with actual rates dependent on the type of solvent and the type of rubber.

Natural rubber has a very high molecular weight and is coupled with variable microgel content. Thus, it reduces the tendency of stacked bales of rubber to flatten out on storage. It means that the rubber has to be mechanically sheared to break down the molecules to a size that enables them to flow without difficulty during processing. Carbonyl groups in natural rubber cross-link prior to coagulation. Cross-linking may be minimized by the addition of 0.15% of hydroxylamine to the latex rendering the rubber soft and be processible.

Natural rubber has the following special features distinguishing it from the synthetic rubber:
1. Ability to crystallize.
2. High resilience
3. Reactivity with oxygen and sulfur

Natural rubber is generally vulcanized using accelerated sulfur systems. Nitroso compounds and their derivatives are also employed.

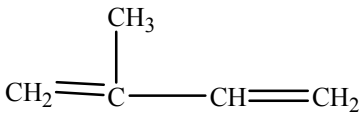
Advantages of Natural Rubber: The major advantage of Natural Rubber, which makes it dominant in many engineering applications, is its dynamic performance. It has a low level of damping, and its properties remain fairly constant over the range 1 to 200Hz, and show only slight increase to 1000Hz. Its combined dynamic properties generally out perform any synthetic rubbers or combinations available to date.

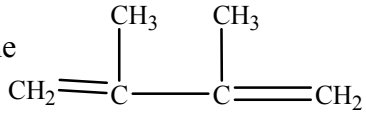
Synthetic Rubbers

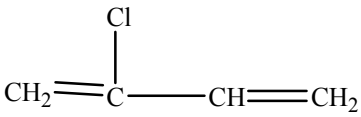
Although natural rubber produced in tropical countries, with the benefit of modern compounding, a useful resource for many applications, it has relatively poor aging properties. Therefore, synthetic materials with matching elastic properties have been developed to replace natural rubber for a wide range of applications.

Polymerization of conjugated dienes leads to the formation of linear polymers containing main chain double bonds. The raw materials used for the preparation of synthetic rubber are:

(a) buta 1,3-diene

(b) Isoprene 

(c) 2,3 dimethyl buta-1,3- diene 

(d) Chloroprene 

A number of elastic materials similar to natural rubber can be made by copolymerizing one of the above monomers.

With the invention of Zieglar Natta catalyst systems, alkyl lithium catalyst systems, it became possible to produce commercially useful materials with properties matching with those of rubber. Synthetic rubbers have the polymer structure with low cis content and as a result the amount of crystallinity that develops during cooling or on stretching is comparatively less than natural rubber.

There is now a wide range of synthetics available which are able to cope with high and low temperatures, contact with fluids of various types (including the contact under high pressures), and aggressive or corrosive environments.

The main synthetic rubbers are outlined below:

(i) Styrene butadiene rubber (SBR)

(ii) Butadiene rubber (BR)

(iii) Isoprene rubber (IR)

(iv) Chloroprene rubber (CR)

(v) Nitrile rubber (NR)

(vi) Ethylene-propylene tetra polymer

(vii) Butyl rubber

Styrene Butadiene Rubber (SBR): Unlike natural rubber, SBR does not break down to any great extent, when subjected to various extreme conditions as encountered during their performance and usage . Natural rubber is crystalline with a T_g of about 50° C whereas SBR with its irregular structure is amorphous. The crystallinity of natural rubber is reduced by creating cross-links and by incorporation of fillers. It still crystallizes on extention and normal ambient temperatures to give a good tensile strength. Vulcanisates are weak and to obtain products with high strength, it is essential to use carbon black as filler. Black-reinforced SBR exhibit a very good abrasion resistance. With oxidation, SBR molecules tend to cross-link leading to a more hard and brittle rubber.

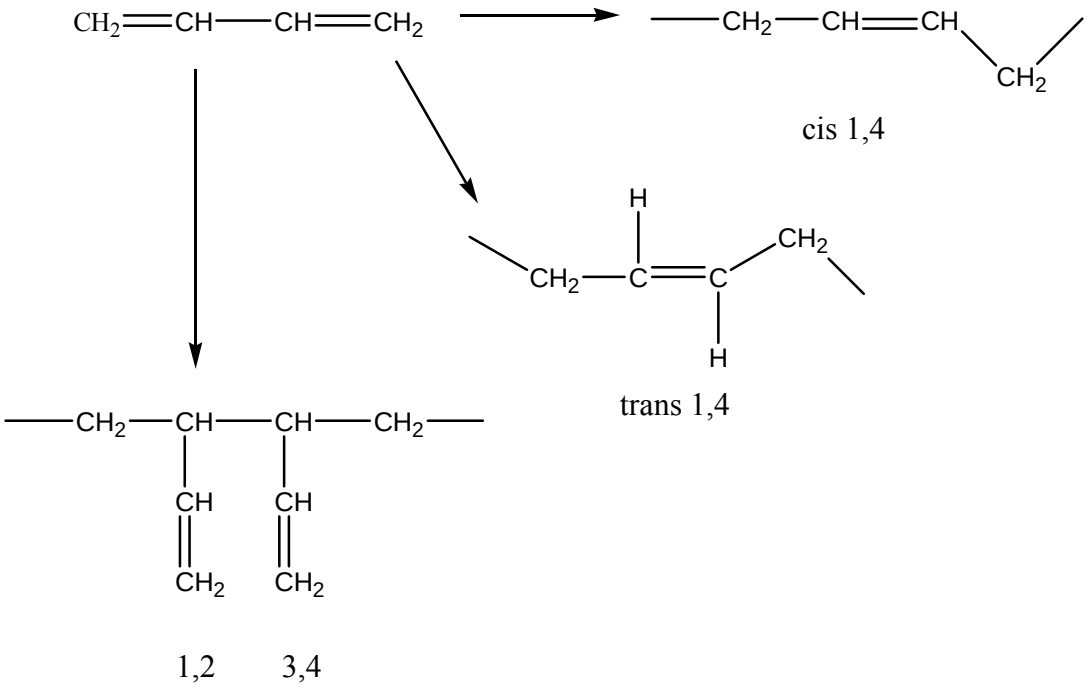
It is a co-polymer of styrene and butadiene. It is an unsaturated hydrocarbon polymer. In 1970s SBR was the world's most important rubber. A general-purpose rubber, which, when compounded with carbon black, behaves like natural rubber or neoprene rubber (Tg is higher at about -55°C). It is quite in demand in the market due to the following reasons:

1. Low cost
2. A high level of product uniformity

Butadiene and styrene can be copolymerized in any proportion. SBR having a content of 23.5 % styrene are rubbery; SBR containing 50% styrene are like leather and SBR containing 70% styrene are like rigid materials.

Butadiene Rubber (BR): Polybutadiene was first prepared in the early 20^{th} Century. In the early methods, butadiene was prepared by sodium catalyzed polymerization and by free radical emulsion polymerization. The butadiene thus prepared did not posses the desired properties. With the development of Zieglar-Natta catalyst systems, polymers containing 90-98% of a cis-1, 4 structures can be produced.

The structure of *cis*-1, 4 polybutadiene is very similar to that of natural rubber. Both materials are unsaturated polymeric hydrocarbons but the double bonds in natural rubber are activated by the presence of methyl groups where as the BRs are less reactive due to the absence of methyl groups. Polybutadiene rubber exhibit higher resilience, and lower heat buildup than natural rubber and thus, find applications in tyre industry. These synthetic rubbers have poor tear resistance, poor tack and lower tensile strength that is why they are always used more commonly in conjunction with other materials which can help achieve desired properties.



(Acrylo) Nitrile Butadiene Rubber (NBR): NBR is a co-polymer of acrylonitrile and butadiene and is prepared by free radical emulsion polymerization. The Acrylonitrile (ACN) content varies from 25 to 50% in NBR since ACN is a non-hydrocarbon monomer, its copolymer attains good resistance to oils and solvents. Increasing the acrylonitrile content, provides an improvement in compatibility with polar plastics like PVC, besides rendering better strength and, hardness properties. These rubbers have a high Tg. Nitrile rubbers, sometimes, are used in conjunction with plastics. Low molecular weight liquid nitrile rubbers with vinyl, carboxyl or mercaptans reactive end groups have been used with acrylic adhesives, epoxide resins and polyesters.

Ethylene Propylene Rubber (EPDM or EPR): This is a commonly used non-polar rubber in applications that require good aging properties, for example, hoses for heaters and radiators, car doors and seals. Moreover, the structure of the polymer can be altered to give a fairly wide range of properties and uses.

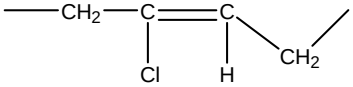
Other more expensive varieties are generally designed to increase the working temperature range, especially for the high-end applications, and usually by incorporation of groups such as fluorine in the carbon backbone for this purpose.

EPDM rubbers are widely used in mechanical goods, wine covering, auto applications and adhesives.

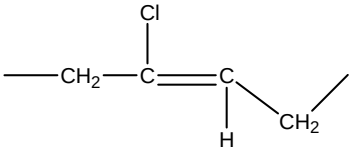
Silicone Rubber: Silicone rubbers are unique polymers without any carbon backbone, but having the units of –Si-O-Si-O-. The extended –Si-O-Si-O- units are useful for their applications at wide temperature range. It has a Tg as low as -127°C depending upon the structure and type of the polymer. They can be used in services at temperature ranges of 200°C or more and that too for several years.

Chloroprene Rubber (CR): Chloroprene rubber, an early synthetic rubber, has been used in many outdoor applications due to its superior weathering properties and oil resistance. It is a polar polymer with improved resistance to attack by non-polar oils and solvents. It has high toughness, good fire resistance, good weatherability, and can easily be bonded to metals. It performs well compared with Natural Rubber in many ways but can suffer from long term stiffening (change in properties) and its low temperature performance is not as good as Natural Rubber.

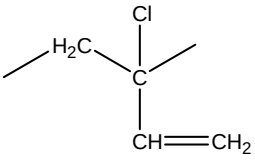
The monomer, 2-chlorobuta-1,3-diene, better known as chloroprene, is polymerized by free-radical emulsion polymerization to give a polymer consisting of trans-1,4-polycloroprene (~ 85%); cis-1,4 polychloroprene (~ 10%), 1,2- polychloroprene (~1.5%) and of 3, 4-polychloroprene (~1%). The methyl group activates the double bond in the polyisoprene molecule, whereas the chlorine group has an opposite effect in polychloroprene. Thus, the polymer is less labile to oxygen and ozone attack. Due to chlorine atoms, the polymer shows improved resistance to oil compared to allyl-hydrocarbon rubbers. The rubbers also have a measure of resistance to burning which is further improved by use of fire retardant. These advantages with a somewhat better heat resistance than the diene hydrocarbon rubbers have resulted in the extensive use of these rubbers.



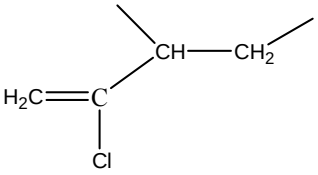
cis-1,4 (85 %)



trans-1,4 (85 %)



1,2 (1.5 %)



3, 4 (1 %)

Ecofriendly Polymers

Advent of polymers and polymeric materials has been responsible for the development of many of the products and devices which otherwise would have remained only at a concept stage. In fact the research efforts in the last 100 years, all over the world, have been dedicated, to a great

extent to develop newer polymeric materials on the one hand while finding the alternatives to the conventional materials by using polymeric materials on the other hand. As a result, for most of the applications, polymers and plastics have replaced the conventional materials like metal, wood, etc. the polymer industry with a vast range of polymeric products has assumed a prime place across the continents. Many of the applications and even the products, which were beyond the imagination, became the reality! The recyclability of plastics besides their non-biodegradable nature have mainly been responsible for the fact that today the plastics have become a house-hold name.

Development of polymers was mainly with the aim to have materials with properties like strength, lightweight, and stability under extreme environmental conditions and durability. Once all the desired characteristics were achieved by designing of wonder (polymers) materials, it become quite obvious for the industries as also for the consumers to exploit such materials. Now, if some one asks making the polymers or plastics as biodegradable, it would obviously sound unrealistic. But the fact remains that today, the need for developing bio-degradable polymers has taken center stage of the research plans of the scientists all over the world. Why such a change of scenario of requirements needs to be understood and appreciated.

There are two main reasons, which are behind the need to develop the biodegradable polymers: (i) environment concerns and (ii) sustainability. The concerns for environment have assumed greater proportions mainly because the proportion of the non-recyclable plastics in the municipal solid waste as well as in the industrial solid waste has been rising and their disposal by landfilling is a burden on the environment. With time, the plastic waste has been growing and to deal with it has already become a major concern for environmentalists. It has become known that the polymers based on halogenated monomers are the potential hazards as they release dioxins (carcinogenic substances) on burning or on heating during recycling. In several countries, the measures are a foot to ban the use of polymers based on halogenated monomers. The inadequate facilities and the absence of environment-friendly practice of waste-management are the reasons due to which the policy makers and regulators are forced to adopt measures, which demand for the degradable plastics. To try and make the materials designed to be non-degradable, as degradable is something that has little logic especially when it is an established fact that the plastics (polyolefinic) for packaging are store house of energy which will be lost on degradation.

The other reason pertains to the sustainability of polymers. The petroleum resources, to manufacture polymers, are not going to be forever and with the existing rates they would deplete faster than expected. Each time the prices of petro- products rise, the viability for alternative renewable materials appears feasible.
When will it become reality is perhaps difficult to predict but what is certain is the fact that the polymers based on renewable resources will be the sustainable option.

To start with, the development of synthetic polymers originated from the knowledge about polymers and polymeric materials from renewable resources suggests that it is possible to develop polymers from renewable resources. However, the challenge is to produce the monomers and then convert them into polymers in an economically feasible way. The important biopolymers are discussed here.

The major classes of biodegradable polymers are discussed here below:

(1) **Poly Lactic Acid (PLA) :** Polylactic acid or Polylactide (PLA) is a biodegradable, thermoplastic, aliphatic polyester derived from lactic acid which can be produced from cornstarch or sugarcane. Bacterial fermentation is used to produce lactic acid, which is oligomerized and then catalytically dimerized to make the monomer for ring-opening polymerization. It can be easily produced in a high molecular weight form through ring-opening polymerization using stannous octoate as catalyst. Polylactic acid has the ability to degrade under aqueous conditions. It is used for biomedical applications such as hydrolyzeable stitches that degrade over time after they are applied to a wound.

There are two types of renewable resources that have significance for polymer industry. One category of products fall in the category where the polymer as such is the output. The prominent examples for this type of renewable resource are starch or polysaccharides. While starch is obtained from products like potato, maize and corn, the polysaccharides (galactomannan) are obtained from guar seeds. Here the polymers are used as such for various applications.

The other category of renewable resources include the products that have the potential to generate monomers which then can be transformed into polymers. The prominent monomers that have been tried so far include lactic acid, glycollic acid, caprolactum, p-dioxanone, hydroxy alkanoate and trimethylene carbonate. All these monomers are obtained from the natural resources by biotic process using either the microbes or the enzymes.

(2) **Starch-based polymers:** Starch is a linear polymer (polysaccaride) made up of repeating glucose groups linked by glucosidic linkages in the 1-4 carbon positions. The length of the starch chains vary with plant source but in general the average length is between 500 and 2 000 glucose units. There are two major molecules in starch - amylose and amylopectin. The alpha linkage of amylose starch allows it to be flexible and digestible.

Starch-based biodegradable plastics may have starch contents ranging from 10% to greater than 90%. These can be based on crops such as corn (maize), wheat or potatoes. As the starch content is increased, the polymer composites become more biodegradable and leave less residues. Often, starch-based polymers are blended with high-performance polymers (e.g. aliphatic polyesters and polyvinyl alcohols) to achieve the necessary performance properties for different applications.

Biodegradation of starch based polymers is a result of enzymatic attack at the glucosidic linkages between the sugar groups leading to a reduction in chain length and the splitting off of sugar units (monosaccharides, disaccharides and oligosaccharides) that are readily utilised in biochemical pathways.

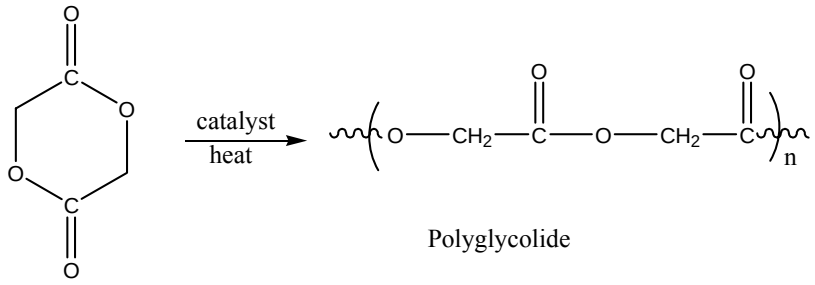
At lower starch contents (less than 60%) the starch particles act as weak links in the plastic matrix and are sites for biological attack. This allows the polymer matrix to disintegrate into small fragments, but not for the entire polymer structure to actually bio-degrade.
There are several categories of biodegradable starch-based polymers including:

- Thermoplastic starch products;
- Starch synthetic aliphatic polyester blends;

- Starch PBS/PBSA polyester blends; and

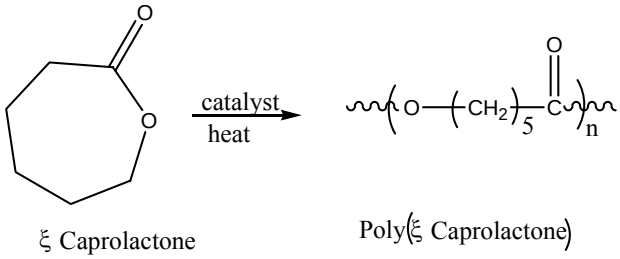
(3) Synthetic biodegradable polymers, such as aromatic aliphatic co-polyesters

a) **Polyglycolide (PGA). :**Polyglycolide is a highly crystalline (45—55%) simplest linear aliphatic polyester with a high melting point (220—225°C) and a glass-transition temperature of 35—40°C. Ring-opening polymerization yields high-molecular-weight materials, with approximately 1—3% residual monomer present.



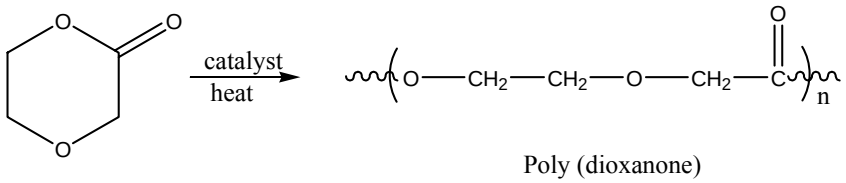
Because of its high degree of crystallization, it is not soluble in most of the organic solvents; the exceptions are highly fluorinated organics such as hexafluoroisopropanol. Fibers from PGA exhibit high strength and modulus and are too stiff to be used as sutures except in the form of braided material. Sutures of PGA lose about 50% of their strength after 2 weeks and 100% in 4 weeks, and are completely absorbed in the body systems in 4—6 months.

b) **Poly (caprolactone).** The ring-opening polymerization of caprolactone yields a semicrystalline polymer with a melting point of 59—64°C and a glass-transition temperature of —60°C .The polymer is tissue compatible and is used as a biodegradable suture. Because the homopolymer has a degradation time of the order of 2 years, copolymers have been synthesized to accelerate the rate of bioabsorption. For example, copolymers of caprolactone with dl-lactide have yielded materials with more-rapid degradation rates. A block copolymer of -caprolactone with glycolide, offers reduced stiffness as compared to pure PGA.



c) **Poly (dioxanone)-** PDO is a polyether-ester having approximately 55% crystallinity, with a glass-transition temperature of —10 to 0°C. This material has The polymer is processed at the lowest possible temperature to prevent depolymerization back to monomer.

Poly (dioxanone) has no acute or toxic effects on implantation. The monofilament loses 50% of its initial breaking strength after 3 weeks providing an advantage for slow-healing wounds.



p-dioxanone

Poly (dioxanone)

Currently, only devices made from homopolymers or copolymers of glycolide, lactide, caprolactone, p-dioxanone, and trimethylene carbonate have been cleared for marketing by FDA. A number of other polymers, however, are being investigated for use as materials for biodegradable devices. In addition to their suitability for medical uses, biodegradable polymers make excellent candidates for packaging and other consumer applications. A number of companies are evaluating ways to make low-cost biodegradable polymers.

(4) Poly hydroxyalkanoates (PHA): Polyhydroxyalkanoates (PHAs), is a family of biodegradable polyesters with attractive properties that could replace many petroleum-based plastics used today.

Polyhydroxyalkanoates (PHAs) are biodegradable polyesters, which are accumulated as carbon/energy storage or reducing power materials in various microorganisms usually under the condition of limiting nutritional elements such as N, P, S, O, or Mg in the presence of excess carbon source.

The mechanical properties of PHAs are highly dependent on the constituting monomer units and molecular weight. Its high melting temperature of 170 ^{o}C makes the processing of P (3HB) difficult. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-co-3HV)] copolymer is less stiff and tougher. P(3HB-co-3HV) copolymer shows higher elongation to break and reduced melting point ranging from 100 ^{o}C to 160 ^{o}C, depending on polymer composition (0-25 mol% 3HV). Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HHx)] and poly(3-hydroxybutyrate-co-3-hydroxyalkanoate) [P(3HB-co-3HA)] have superior mechanical properties similar to low density polyethylene (LDPE) depending on the monomer composition.

Various microorganisms such as *Ralstonia eutropha, Alcalgenes latus, Pseudomonas* sp*are known* to produce PHAs by the condensation or modification of acetyl-CoAs generated from sugars.

E. coli is used to convert sugars based from renewable resources into a family of broadly useful polymers at greatly increased yields. Polyhydroxyalkanoates (PHAs), is a family of biodegradable polyesters with attractive properties that could replace many petroleum-based plastics used today.

Proctor & Gamble has developed a family of PHAs . P&G's resin, called Nodax™ which can be converted to films and sheets, moulded articles, fibres, elastics, laminates and coated articles, nonwoven fabrics, synthetic paper products, and foams. It has properties similar to a polyolefin and surface properties much like PET, including receptivity to printing inks and dyes. Nodax™ biodegrades aerobically and anerobically (e.g., under water) and is alkaline digestable and water soluble.

Dyes

Introduction : A dye is a colored substance that can be applied in solution or as a dispersion in a substrate giving it a colored appearance. The substrate maybe textile fibers, paper, leather, hair, fur, plastic material, wax, a cosmetic base or even food products. The dye possesses a natural affinity for the substrate and is readily absorbed from solution under suitable conditions of temperature and pressure. Simple chemical reactions such as nitration, reduction, halogenation, sulphonation, oxidation, carboxylation and amidation are used for synthesizing dyes.

The dye is usually used as an aqueous solution, and may sometimes require a mordant to improve the fastness of the dye on the fiber. Dye is also used to color various products meant for different applications and uses such as drugs and pharma, cosmetics and personal care, processed food and farm products, etc.

Color and constitution : All the dye substances are capable of absorbing radiant energy of a characteristic frequency in the visible range of the spectrum. Substances like benzene, which absorb in the UV region and that is why they appear colorless. Substances such as acetone which, absorb in IR region also appear colorless. It is only the substances, which, absorb light in the visible region, appear colored and dyes are the prominent ones in this category of substances.

The color of an organic dye is associated with the presence of certain groups of atoms called chromophores, for example unsaturated groups such as the nitro ($-NO_2$), nitroso (N=O), azo (N≡N), ethylene ($CH_2=CH_2$), carbonyl groups (-C=O), etc. Compounds containing these groups are called chromogens. Chromogens can easily be substituted by weakly acidic or basic groups such as $-NH_2$, $-NH(CH_3)$, $-N(CH_3)_2$, -OH . The presence of such groups increases the color yielding power of a chromophore and are known as auxochromes.
Presence of single chromophoric group may not be sufficient to produce color but if two or three such groups are present in a conjugated system, color usually appears in a compound. A few notable chromophores are shown in **Fig XXXVI**.

Thus acetone, (CH_3COCH_3), is colorless whereas the diketone (CH_3-CO-CO-CH_3) is yellow. A single C=C does not produce color but if a number of them are present, the color appears. Ethylene, ($CH_2=CH_2$), is colorless, whereas hexa-octene $CH_3(CH=CH)_6CH_3$ is yellow.

Chromophores produce color in compounds by introducing the possibility of resonance involving charged structures. Effect of auxochromes increases the intensity of color by giving rise to new charged canonical structures by enhancing resonance. Deepening of color on

increasing the conjugation in the molecule is due to increase in the number of electrons involved in oscillation.

Thus auxochromes serve two purposes:

1. Increase intensity of color by bringing a shift from the ultra-violet into the visible portion of the spectrum
2. Enhancing the capacity of the chromogen to fix to the fabric or material to be dyed either by association or salt formation. In other words, auxochromes turn the chromogen into a dye.

Concept of color of dyes: A colored compound is built up from three subsystems, namely an auxochrome and a chromophoric group linked together by a system of conjugated double bonds (including aromatic groups). Auxochromes are electron donors and chromophores are electron acceptors.

In the spectrum of electromagnetic radiation, the microwave (wavelength above 500 μm), infrared (0.7-500 μm), visible (400-700 nm), and ultra-violet (10-400 nm) regions are important in chemistry, because the molecules, by absorbing energy are raised to excited states. Absorption of the relatively low energy microwave and infra-red radiation is associated with changes in the rotational and vibrational energy of molecules and atomic groups. However, the higher energy of visible and ultra-violet light raises the electrons to the excited state leading to the electronic spectra.

Dyes are characterized in accordance with their capacity to absorb the energy of that part of the electromagnetic radiation to which the eye is sensitive. What is not absorbed by the dye is what we see. The color of the dye, therefore, corresponds to the wavelength of the light reflected by the dye.

A dye molecule consists of a chromophoric system in which the chromophore forms part of a conjugated chain of single and double bonds , terminating in a polar atom or group which is the auxochrome. There maybe two polar terminal groups in a complex dye and transition from one to the other takes place through an electron surge through the conjugated chains.
When light of appropriate frequency falls on the molecule, the oscillating electrons permit the absorption of energy causing a transition from ground to excited state.

$E = E_{excited} - E_{ground.} = h\nu$

Thus, by absorption of light, electrons are raised from a state of lower energy to higher energy and the difference in energy levels between the two states determine the wavelength of light absorbed and the observed color of the dye corresponds to its complement.

The smaller the difference in energies, lower the energy absorbed and hence lower is the frequency or larger is the wavelength. Thus, any factor, which decreases the energy, shifts the absorption to longer wavelength. Resonance lowers the energy of a molecule but if resonance occurs amongst charged structures, then energy of both ground as well as excited state is lowered. Since the charged structures contribute more to the excited state, the energy of the excited state is lowered to a greater extent than the ground state. In other words, resonance

amongst charged structure lowers energy and shifts absorption to longer wavelength.

Let us consider the case of benzene. The two major structures are two Kekule structures **(Fig XXXVII)**. In addition, a number of charged canonical structures can also be written but they contribute relatively little to either the ground or excited state and thus, benzene absorbs in the UV region.

In nitrobenzene, the contribution due to the charged structures is more than that of benzene; consequently, the absorption is shifted to a longer wavelength (blue) thereby producing a pale yellow color which is the complementary color to blue **(Fig XXXVIII)**.

In p- nitro aniline, the charged structures contribute still more and thus, it is deeper in color. The large contribution by charged structures to the resonance hybrid of quinone explains their color **(Fig XXXIX)**.

Classification of dyes: Dyes and pigments can be classified as according to chemical structure as well as according to their application methodology. The most important commercial products are known based on their characteristic chromophore groups such as the azo, anthraquinone, sulfur, indigoid, triphenyl methane and phthalocyanine dyes.

The concept of dyeing started with the dyeing of wool in 415 BC. In the early days from 115 BC to the 18^{th} century, natural materials such as molluscs, lichen, insects and plants are used for dyeing. In 1856, the first synthetic dye 'Mauve' was discovered followed by the discovery of the dye Magenta in 1858. This led to the formation of a new industry and now 'dyeing' is considered as an important method for value-addition of products. .

Pre-historic man had already dyed furs, textiles and other substances, using not only of vegetable origin but also of animal origin. Further developments led to the development of various dyeing processes and high quality dyes. Indigo obtained from Indigofon tinctoria, ancient purple obtained from the purple snail, alizarin obtained from madder canpeache wood are examples. The first synthetic organic dye was discovered by Perkin. The elucidation of the structure of benzene and the quadric valence of carbon in the 18^{th} century led to the preparation of synthetic dyes.

Chemical classification: Dyes are classified by chemical structure, which helps in the identification of dyes having characteristic properties. Based on chemical structure, the dyes may be aza – anthraquinone and aza – annulene type.

(a) **Azo dyes:** Azo dyes may contain one, two or three azo groups (-N=N-). The azo group is attached to two radicals of which one or both may be aromatic. The nitrogen atoms in the azo group are sp^2 hybridized. Some examples of azo dyes are solvent yellow, disperse red, disperse blue, direct green, direct black, etc.

(b) **Anthraquinone dyes**: This is an important class of dyes, which has been used since ancient times; in the wrappings of mummies in Egypt. Anthraquinone dyes are based on 9,10 – anthraquinone. The dyes are essentially colorless but characterized by brightness

and good fastness properties, including light fastness.

(c) **Polycyclic Aromatic Carbonyl compounds:** These dyes contain one or more carbonyl groups linked by a quinonoid system. They are relatively large molecules built up from smaller units, typically anthraquinones. Polycyclic aromatic carbonyl dyes are available in the entire shade. The dyes are characterized by good light fastness and wet fastness. The absence of electron donating and electron withdrawing groups other than carbonyl restricts the number of photochemical sites in the molecule.

(d) **Indigoid dyes**: The indigoid dyes are also characterized by the presence of carbonyl groups. Indigo is the blue dye used almost exclusively for dyeing denim jeans and jackets.

(e) **Di and Triaryl Carbonium and related dyes:** The dyes are bright and strong, but are generally deficient in lightfastness. They are used in outlets where brightness and cost – effectiveness, rather than performance, are paramount. These are especially derivatives of pyronines (xanthenes).

(f) **Phthalocyanines:** Phthalocyanines dyes are analogues of natural pigments like chlorophyll and heme. Unlike these natural pigments, which have extremely poor stability, phthalocyanines are probably the most stable. Substituents can extend the absorption to longer wavelengths, but not to shorter wavelengths, and therefore their hues are restricted to blue and green. They are used extensively in printing inks and paints.

(g) **Sulfur dyes:** These dyes are synthesized by heating aromatic amines, phenols or nitro compounds with sulfur or, more usually, alkali polysulfides. They consist of macromolecular structures of the phenothiazone type, in which the sulfur is present as a bridging link. These dyes are used for dyeing cellulosic fibres. They are insoluble in water and reduced to the water –soluble leuco form for application to the substrate by using sodium solution.

(h) **Nitro and Nitroso Dyes:** These dyes are weak dyes used for dyeing the natural animal fibres such as wool and silk. They were nitro derivatives of phenols e. g., picric acid or naphthols. They are cost effective because of their easy synthesis from inexpensive intermediates. Nitroso dyes are metal –complex derivatives of o-nitrosophenols or naphthols.

Classification based on use

Reactive Dyes: Reactive dyes are colored compounds that react with the textile fibers to form covalent bonds. It utilizes a chromophore containing a substituent that is capable of directly reacting with the fibre substrate. The covalent bonds that attach reactive dye to natural fibers make it among the most permanent of dyes. The functional groups of fibers that react with reactive dyes to form covalent bonds are the hydroxyl group of cellulose and the amino, carboxyl, hydroxyl and thiol groups of wool and silk. Most of the Anthraquinone reactive dyes are derived from bromamine acid. These dyes give a bright shade and excellent lightness.

Disperse Dyes: Disperse dyes were originally developed for the dyeing of cellulose acetate, and are substantially water insoluble. The dyes are finely ground in the presence of a

dispersing agent and then sold as a paste, or spray-dried and sold as a powder. In some cases, a dyeing temperature of 130 °C is required, and a pressurised dyebath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fibre.

Acid Dyes: Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dyebaths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups of the dye and groups in the fiber. For e.g. Picric acid and Martius yellow **(Fig XL)**.

Acid dyes give brilliant reds, violets, blues and greens. They exhibit excellent light fastness. Acid dyes may be classified into two groups

1) Bromamine acid Derivatives
2) Quinizarin Derivatives

Vat Dyes: Vat dyes have been used to dye cotton and other cellulose fibers. Vat dyes are of anthraquinone type. They are converted to leuco compounds by reducing agents such as sodium hydrosulfite in alkaline conditions. These water-soluble lecuo compounds have an affinity to cellulose fibers and hence, they easily penetrate into the fiber matrix. After application, on oxidation either by air or by some oxidizing agents, the dye becomes water – insoluble again and fixes firmly onto the fiber. The anthraquinone vat dyes can be classified into several groups on the basis of their chemical structures.

Mordants: Mordants are substances of organic or inorganic origin, which combine with the coloring matter and are used to fix dyes onto the substrate. The mordant substances include acids such as tannic acid, oleic acid and stearic acid, etc.; and metallic substances such as various combinations or soluble salts of chromium, aluminum, iron, copper, and tin. Mordant improves the fastness of the dye on the fiber.

The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool mainly for black and navy blue shades. The mordant, potassium dichromate, is applied as an after-treatment.The most commonly used mordant dyes have hydroxyl and carboxyl groups and are negatively charged, i.e. they are anionic. It is often noted that when a mordant dye forms a complex with a metal, there is a strong color change. This is because metals have low energy atoms. The incorporation of these low energy atoms into the delocalised electron system of the dye causes a bathochromic shift in the absorption. It is this delocalised electron system which is fundamentally responsible for color in dyes. Since different metal atoms have differing energy levels, the color of the complex may also differ and thus, one can produce variety of colors on the dyed surfaces.

Direct dyes: Compounds, which are able to dye cellulose fibers without any acids are called substrating or direct dyes. The name 'direct dye' refers to the fact that these dyes can be used directly. They are almost always azo dyes, with some similarities to acid dyes. Direct dyes have a chemical affinity for the fiber and are used to dye cotton, linen and rayon. They are easy to apply and come in a wide range of colors. The colors of direct dyes are duller and the wash fastness is poorer than those provided by fiber-reactive dyes,. The colors can be made wash- fast by appropriate treatment. One of the advantages is that direct dyes may be more light-fast, which means that they are more resistant to fading in the light, than fiber-reactive

dyes.
Dyeing, using direct dyes is normally carried out in a neutral or slightly alkaline dyebath with the addition of either sodium chloride (NaCl) or sodium sulfate (Na_2SO_4). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. The water solubility of the dye depends on the presence of the sulphonate group in the dye molecules. More the sulphonate groups, more is the water-solubility. The two important direct dyes are described below:

Malachite Green Dye
The dyes are salts of amino or hydroxyl derivatives of compounds of the Triphenylmethanol type. Only di- and tri- substituted derivatives are of commercial importance. Also amino and hydroxyl groups should be on different rings in para- position to methane carbon atom

Preparation of Malachite Green dye: Benzaldehyde is refluxed with slight excess of dimethylaniline in the presence of HCl or H_2SO_4 with $ZnCl_2$ and condensed. This leads to the formation of a leuco base **(Fig XLI)** with the excess dimethylaniline. The excess dimethylaniline is removed by steam distillation and the solution is made alkaline. Leuco base is oxidized to carbinol base by PbO_2. Lead formed due to the reduction of PbO_2 is removed and carbinol base is made into dye salt by addition of HCl **(Fig XLII)**.

Congo Red Dye
Congo Red dye belongs to the class of azo dyes and was the first dye to become of commercial value for dyeing cotton.

Preparation of Congo Red dye: Congo red is made by coupling tetrazotized benzidine with two molecules of naphthionic acid **(Fig XLIII)**.

Action: Congo red is used in the form of its sodium salt. The solution is red in color and used directly for dyeing cotton. It is highly sensitive to light and acids. It is an important laboratory indicator because of its sensitivity to acids. It is blue at pH<3 and red at pH>3. The deepening of color under strong acidic conditions is due to resonance stabilized charged canonical structures **(Fig XLIV)**.

Alizarin Dye
Preparation of Alizarin dye: Alizarin was obtained by acid hydrolysis of ruberythric acid and identified as 1,2-dihydroxyanthraquinone **(Fig XLV)**. Mild oxidation of alizarin yields purpurin, which is of purple color **(Fig XLVI).**

Alizarin finds its applications in dying and printing processes, it is used either as an aqueous suspension or as a water-soluble bisulfite compound. It is used with many different mordants; Al^{3+}-red, Fe^{2+}- deep violet, Fe^{3+}- brownish black, Sn^{2+}- reddish violet, Cr^{3+}- brownish violet, Mg^{2+}- violet and Ba^{2+}- blue.

Indigo Dye
It is the earliest vat dye obtained from indigofera. Indigo is applied to wool using mild alkaline conditions with addition of glue or suitable colloidal material to protect the wool. Wool is dyed at 40-60 °C. It is moderately fast to light but the greater advantage of indigo is

that there is little or no change in color intensity even after a long period of usage of dyed fabric.

Preparation of Indigo dye: The coloring component is present as glucoside of indoxyl called indican **(Fig XLVII)**. Indican is hydrolyzed by an enzyme to free indoxyl. Indoxyl on oxidation gives indigotin or indigo. Air oxidation of indoxyl produces indigo by free radical mechanism **(Fig XLVIII)**.

Action : Indigo exists in the cis and trans forms. On storage, cis form rapidly changes to trans form **(Fig XLIX)**. Indigo is insoluble in water as well as organic solvents. To explain the deep blue color of indigo, it is believed that there is a tetrapolar structure, which is highly conjugated **(Fig L)**. It is also believed that the deep blue color is due to resonance between following structures **(Fig LI)**. Indigo is a dark colored powder. It can be reduced by alkaline sodium hyposulfite to a colorless form called indigotin white. It is soluble in alkali. It is indigotin white, which is applied to the fabric and converted to indigo by oxidation **(Fig LII)** leading to the blue color.

Methyl Orange Dye

This dye is used as an indicator. Methyl orange is obtained as an orange colored product with fine particles. It is not water-soluble and can be easily recrystallized. It has no sharp melting point.

Preparation of Methyl Orange dye: The diazonium salt of sulphanilic acid is coupled with N, N- dimethyl aniline **(Fig LIII)**. Sulphanilic acid is sparingly soluble in water and exists as a zwitter ion. Coupling is done in acetic acid and not in HCl because HCl being a strong acid will form N, N dimethylanilinium salt that does couple.

Action: Methyl orange is sensitive to acids and is therefore used as a dye but as an indicator in acid base titrations. Methyl orange is yellow at pH>4.4 and red at pH<3. 1 **(Fig LIV)**.

Fluorescien Dye

Fluorescien dye belongs to the class of Xanthene dyes. The dyes of this group are based on Xanthene, the chromophore being the Xanythlium ion and the auxochromes being amino or hydroxyl groups meta to the oxygen atom. The xanthene shades range from yellow through violet, the most important shades being red and pink. They are used for the dyeing of cellulosic fibers, wool and silk and for the production of various brilliant insoluble lakes such as phosphomolybdotungstic acid.

The dyes of this group are classified as :

a) Pyronines
b) Saccharines and succireines
c) Rosamines
d) Rhodamines
e) Rhodoles
f) Phthaleins

Preparation of Fluorescien dye: It is prepared by fusion of phthalic anhydride or chlorinated phthalic anhydride with two moles of resorcinol in the presence of anhydrous $ZnCl_2$ at 180°C **(Fig LV)**. The product is isolated by boiling off with water and small amount of HCl. Fluorescien is not used to an appreciable extent as a textile dye due to its light fastness. It is used as a water tracer dye, since its green fluorescence is visible at dilutions as high as 40, 000, 000 times in water.

Action : It is a red brick colored dye and is isolated in the form of powder. It is insoluble in water and soluble in alcohol. It dissolves in NaOH to give reddish brown solution, which on dilution imparts yellowish-green fluorescence. The yellowish green color is due to the formation of a dianion **(Fig LVI)**.

It has a strong green fluorescence in solution even at high dilutions thus it is used in:

- Tracing course of underground water supply.
- Saving life at sea
- Detection of weak circulation of blood.

Crystal Violet Dye

Crystal violet dye belongs to the class of triarylcarbonium dyes. It is soluble in water; a violet dye used for dying silk, wool and mordanted cotton. It is not fast to light.

Preparation of Crystal Violet dye: It is a hexamethyl derivative of pararosaniline. The synthesis of crystal violet starts from dimethylaniline. Dimethylaniline on reaction with carbonyl chloride in the presence of $ZnCl_2$ gives Michler's ketone **(Fig LVII)**. It is then condensed with another molecule of dimethylaniline in presence of $COCl_2$ to give crystal violet **(Fig LVIII).**

Action : In weakly acidic medium, it gives purple color. In strongly acidic medium, it gives green color. In a very strong acidic medium, it gives yellow color **(Fig LIX)**.

This can be explained on the basis of contribution of the resonating structures. We know that deepening of color is due to increase in resonance. The oscillating charge of resonating structures should be in one plane.

In weakly acidic solution, crystal violet exists as a singly charged ion. Here, all the rings are not planar. Only two- thirds of the charge can oscillate in the horizontal direction. Hence it imparts purple color.

In strongly acidic medium, more H^+ ions are there and the dye exists as a doubly charged ion. The entire charge oscillates in horizontal direction. Therefore the color deepens. In very strongly acidic conditions, protonation of the third hydrogen also takes place and the dye exists in the form of ion (III) with three charges. There is no scope of oscillation and therefore very little resonance is possible. The color therefore becomes light.

Phenolphthalein

Phenolphthalein is a white crystalline solid, insoluble in water and is an important acid base indicator.

Preparation of phenolphthalein: Phenolphthalein is prepared by heating one mole of phthalic anhydride with two moles of phenol **(Fig LX)**.

Action: Phenolphthalein is colorless at pH< 8.5 and pink at pH=10. In strongly alkaline conditions, it is colorless because it is slowly converted to the carbinol structure. Below pH 8.5, it exists in a lactone structure, which is colorless. Around pH 10; it exists as a dianion and is pink **(Fig LXI)**.

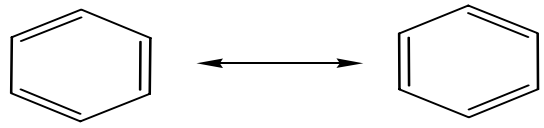


Fig XXXVII: Two basic kekule structure of benzene

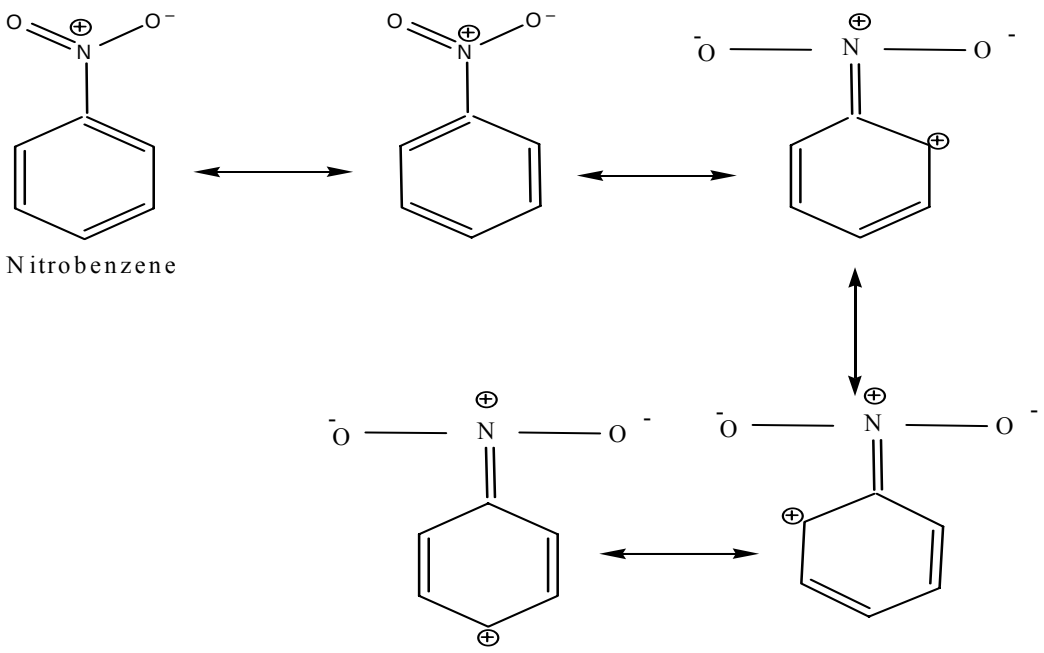


Fig XXXVIII: Charged structures of nitrobenzene. Due to high degree of resonance, absorption is shifted to longer λ and hence, the compound produces color.

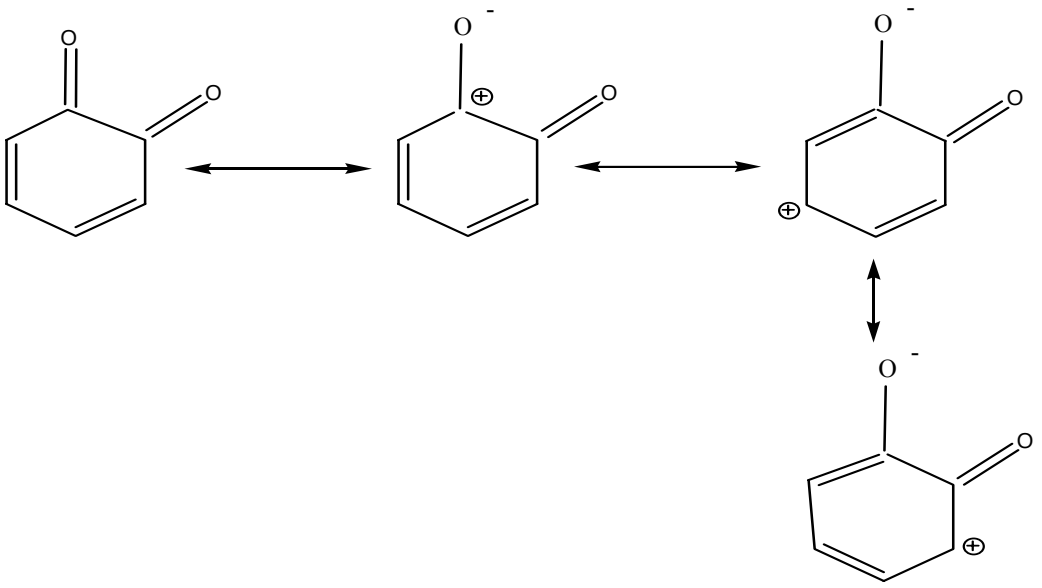
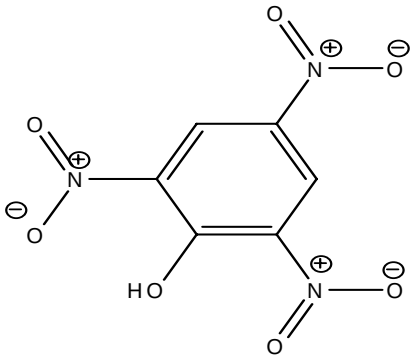
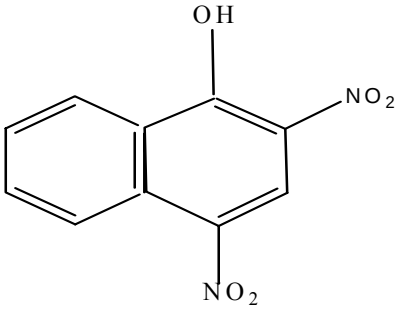


Fig XXXIX: Resonance hybrid state of quinone, which is responsible for the color



Picric acid



Martius Yellow

Fig XL: Examples of acid dyes

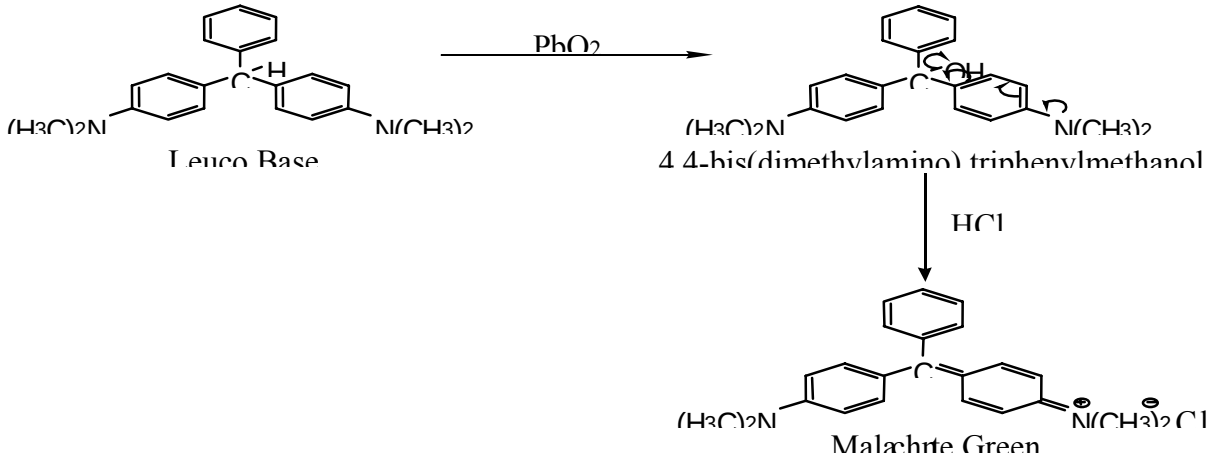


Fig XLII: Leuco base is converted into malachite green dye using lead oxide

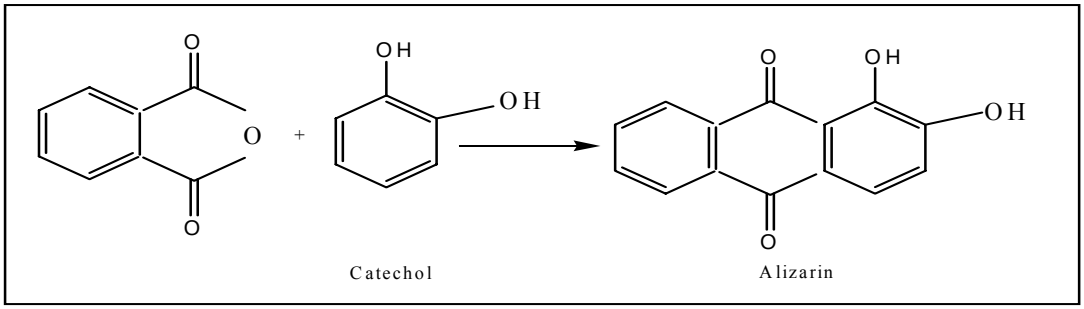


Fig XLV: Synthesis of Alizarin dye using pthalic anhydride

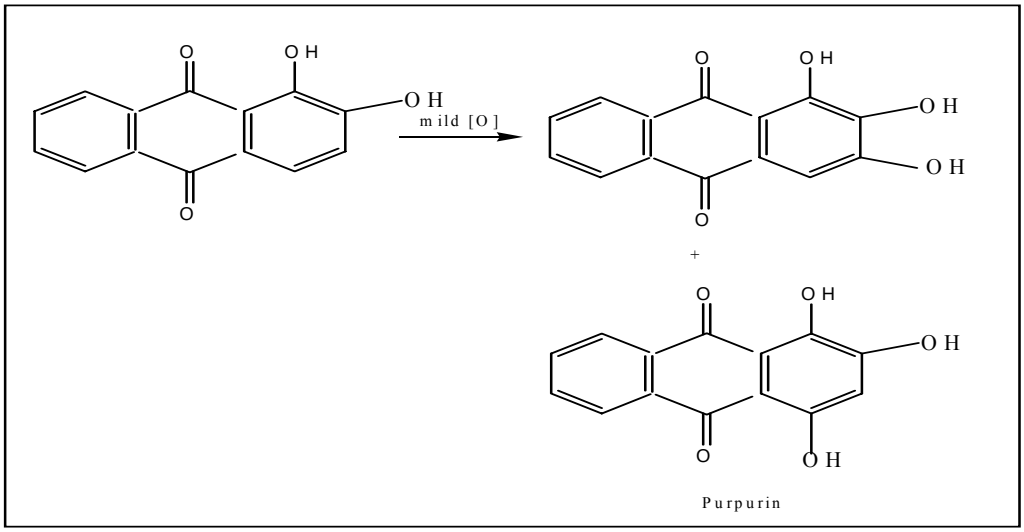


Fig XLVI: Alizarin under mild condition yields purpurin.

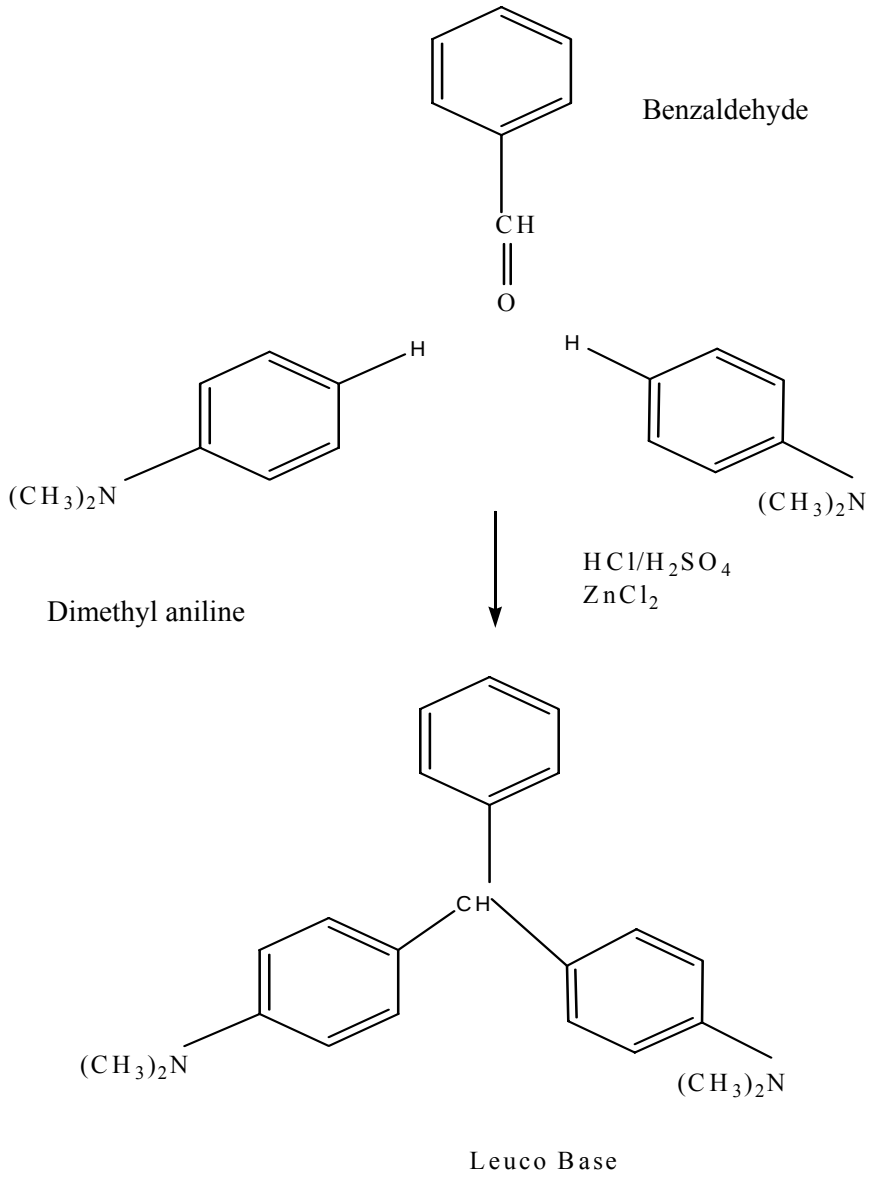


Fig XLI: Reaction of benzaldehyde and dimethyl aniline to produce a leuco base dye.