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Module 4: Polymers

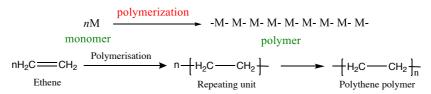
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Module outline: Basic concepts of polymer Blends and composites. Conducting and biodegradable polymers Preparations and applications of some industrially important polymers (Buna N, Buna S, Neoprene, Nylon 6, Nylon 6,6, Terylene). General methods of synthesis of organometallic compound (Grignard Reagent) and their applications in polymerization.

4.1. INTRODUCTION

Probably no group of synthetic compounds is more important to modern life than synthetic polymers. A **polymer** is a large molecule made by linking together repeating units of small molecules called **monomers**. The process of linking them together is called **polymerization**.



Unlike small organic molecules, which are of interest because of their *chemical* properties, these giant molecules are interesting because of their *physical* properties, which make them useful in everyday life. Some synthetic polymers resemble natural substances, but most are quite different from those found in nature. Such diverse items as photographic film, compact discs, rugs, food wrap, artificial joints, Super glue, toys, bottles, weather stripping, automobile body parts, shoe soles, and condoms are made of synthetic polymers. The relevant example of polymer is human chain formation (polymer) which is generated by systematic assembly of humans (monomer).

Polymers can be divided into two broad groups: **synthetic polymers** and **biopolymers** (natural polymers). Synthetic polymers are synthesized by scientists, whereas biopolymers are synthesized by organisms. Examples of biopolymers are DNA, the storage molecule for genetic information—the molecule that determines whether a fertilized egg becomes a human or a honeybee; RNA and proteins, the molecules that induce biochemical transformations; and polysaccharides.

Humans first relied on *natural polymers* for clothing, wrapping themselves in animal skins and furs. Later, they learned to spin natural fibers into thread and to weave the thread into cloth. Today, much of our clothing is made of *synthetic polymers* (e.g., nylon, polyester, polyacrylonitrile). Many people prefer clothing made of natural polymers (e.g., cotton, wool, silk), but it has been estimated that if synthetic polymers were not available, all the arable land in the United States would have to be used for the production of cotton and wool for clothing.

The first **plastic**—a polymer capable of being molded—was celluloid. Invented in 1856 by Alexander Parke, it was a mixture of nitrocellulose and camphor. Celluloid was used in the manufacture of billiard balls and piano keys, replacing scarce ivory. The invention of celluloid provided a reprieve for many elephants, but caused some moments of consternation in billiard parlors because nitrocellulose is flammable and explosive. Celluloid was used for motion picture film until it was replaced by cellulose acetate, a less dangerous polymer.

The first synthetic fiber was rayon. In 1865, the French silk industry was threatened by an epidemic that killed many silkworms, highlighting the need for an artificial silk substitute. Louis Chardonnet accidentally discovered the starting material for a synthetic fiber when, while wiping up some spilled nitrocellulose from a table, he noticed long silk like strands adhering to both

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the cloth and the table. "Chardonnet silk" was introduced at the Paris Exposition in 1891. It was called *rayon* because it was so shiny that it appeared to give off rays of light.

The first synthetic rubber was synthesized by German chemists in 1917. Their efforts were in response to a severe shortage of raw materials as a result of blockading during World War I. Hermann Staudinger was the first to recognize that the various polymers being produced were not disorderly conglomerates of monomers, but were made up of chains of monomers joined together.

Polymer chemistry is part of the larger discipline of **materials science**, which involves the creation of new materials to replace metals, glass, ceramics, fabrics, wood, cardboard, and paper. Polymer chemistry has evolved into a multibillion-dollar industry. Currently, there are approximately 30,000 patented polymers in the United States. More than 2.5×10^{13} kilograms of synthetic polymers are produced in the United States each year, and we can expect many more new materials to be developed by scientists in the years to come.

4.2. CLASSIFICATION OF POLYMERS

On the basis of different chemical structures, physical properties, mechanical behavior, thermal characteristics, stereochemistry etc. Polymers can be classified into following ways:

4.2.1. Classification Based on Source

1. Natural polymers: These polymers are found in plants and animals. Examples are proteins, cellulose, starch, resins and rubber.

2. Semi-synthetic polymers: Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the usual examples of this sub category.

3. Synthetic polymers: A variety of synthetic polymers as plastic (polythene), synthetic fibres (nylon 6,6) and synthetic rubbers (Buna – S) are examples of man-made polymers extensively used in daily life as well as in industry.

4.2.2. Classification Based on Structure

1. Linear polymers: These polymers consist of long and straight chains. The examples of Polymers are high density polythene, polyvinyl chloride, etc. These are represented as:



2. Branched chain polymers: These polymers contain linear chains having some branches, e.g., low density polythene. These are depicted as follows:



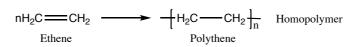
3. Cross linked or network polymers: These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains, e.g. bakelite, melamine, etc. These polymers are depicted as follows:



4.2.3. Classification Based on Mode of Polymerisation

Polymers can also be classified on the basis of mode of polymerisation into two sub groups.

1. Addition polymers: The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds, e.g., the formation of polythene from ethene and polypropene from propene. However, the addition polymers formed by the polymerisation of a single monomeric species are known as homopolymers, e.g., polythene.



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

2. Condensation polymers: The condensation polymers are formed by repeated condensation reaction between two different bifunctional or tri-functional monomeric units. In these polymerisation reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. The examples are terylene (dacron), nylon 6, 6, nylon 6, etc. For example, nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipicacid.

E-Content: Polymers $n NH_2(CH_2)_6NH_2 + n HOOC(CH_2)_4COOH \xrightarrow{-n H_2O} (NH(CH_2)_6NHCO(CH_2)_4CO)_n$ Nvlon 6. 6

4.2.4. Organic and Inorganic Polymers

A polymer whose backbone chain is essentially made of carbon atoms is termed as organic polymer. Monomers of organic polymers are organic compounds. The majority of natural and synthetic polymers are organic polymers. Polystyrene, Poly Methyl Metha Acrylate etc. are common examples of Organic polymers.

Inorganic polymers are those in which atoms other than carbon form the backbone chain of the polymer. Polysiloxanes, Poly dimethyl siloxane are the examples of inorganic polymers.

4.2.5. Classification Based on Molecular Forces

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

1. Elastomers: These are rubber like solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are buna-S, buna-N, neoprene, etc.

2. Fibres: Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

4.2.6. Classification Based on Action of Heat

1. Thermoplastic polymers: These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.

2. Thermosetting polymers: These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldelyde resins, etc.

4.2.7. Classification Based on Tacticity

It is the relative stereochemistry of adjacent chiral centers within a macromolecule.

Isotactic: Functional groups on same side of backbone. e.g. Poly-cis-isoprene.

Syndiotactic: Functional groups on alternating sides of backbone. e.g. Poly-trans-isoprene.

Atactic: Functional groups are randomly distributed around backbone. e.g. Polypropylene.

ξ H-C-H H-C-Ph H-C-H H-C-H	$\begin{cases} \\ H-C-H \\ H-C-Ph \\ H-C-H \\ Ph-C-H \\ H-C-H \\ H-C-H \\ H-C-H \\ Ph-C-H \\ Ph-C-H \\ H-C-H \\ H-C-H \\ H-C-Ph \\ \zeta \\ \end{bmatrix}$	$\begin{cases} \\ H-C-H \\ Ph-C-H \\ H-C-H \\ H-C-Ph \\ H-C-H \\ Ph-C-H \\ H-C-H \\ Ph-C-H \\ H-C-H \\ H-C-H \\ H-C-H \\ H-C-H \\ H-C-H \\ H-C-Ph \\ L \end{cases}$
کی Isotactic	Syndiotactic	ک Atactic

4.2.8. Classification Based on Growth Polymerisation

The addition and condensation polymers are nowadays also referred as chain growth polymers and step growth polymers depending on the type of polymerisation mechanism they undergo during their formation.

4.3. TYPES OF POLYMERIZATION REACTIONS

There are two broad types of polymerisation reactions, i.e., the addition or chain growth polymerisation and condensation or step growth polymerisation.

4.3.1. Addition Polymerisation or Chain Growth Polymerisation

The monomers used most commonly in chain-growth polymerization are ethylene (ethene) and substituted ethylenes. In the chemical industry, monosubstituted ethylenes are known as **alpha olefins**. Polymers formed from ethylene or substituted ethylenes are called **vinyl polymers**.

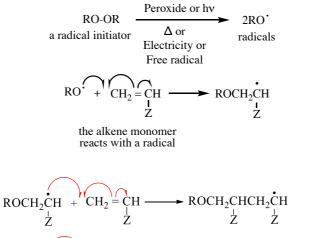
Chain-growth polymerization proceeds by one of three mechanisms: **radical polymerization**, **cationic polymerization**, or **anionic polymerization**. Each mechanism has three distinct phases: an *initiation step* that starts the polymerization, *propagation steps* that allow the chain to grow, and *termination steps* that stop the growth of the chain. We will see that the choice of mechanism depends on the structure of the monomer *and* the initiator used to activate the monomer.

1. Radical Polymerization

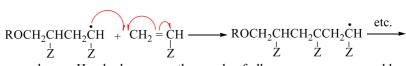
For chain-growth polymerization to occur by a radical mechanism, a radical initiator must be added to the monomer to convert some of the monomer molecules into radicals. The initiator breaks homolytically into radicals, and each radical adds to an alkene monomer, converting it into a radical. This radical reacts with another monomer, adding a new subunit that propagates the chain. The radical site is now at the end of the most recent unit added to the end of the chain. This is called the **propagating site**.

The free radical takes place in the presence of HELPR [H: Heat (≥500 °C), E: Electricity, L: Light (hv: sun light), P: Peroxide, R: Radical (free radical)]. The process is known as initiation of free radical reaction.

Chain-initiating steps



Chain-propagating steps



This process is repeated over and over. Hundreds or even thousands of alkene monomers can add one at a time to the growing chain. Eventually, the chain reaction stops because the propagating sites are destroyed. Propagating sites can be destroyed when two chains combine at their propagating sites; when two chains undergo *disproportionation*, with one chain being oxidized to an alkene and the other being reduced to an alkane; or when a chain reacts with an impurity that consumes the radical.

Three ways to terminate the chain

chain combination

$$2RO - \left[CH_{2}CH\right]_{n}CH_{2}\dot{C}H \longrightarrow RO - \left[CH_{2}CH\right]_{n}CH_{2}CHCHCH_{2}\left[CHCH_{2}\right]_{n}CH_{2}CHCHCH_{2}\left[CHCH_{2}\right]_{n}CH_{2}CH$$

Thus, *radical polymerizations* have chain-initiating, chain-propagating, and chain terminating steps similar to the steps that take place in the radical reactions.

2. Cationic Polymerization

In cationic polymerization, the initiator is an electrophile that adds to the alkene, causing it to become a cation. The initiator most often used in cationic polymerization is a Lewis acid, such as BF_3 or $AlCl_3$ The advantage of such an initiator is that it does not have an accompanying nucleophile that could act as a chain terminator, as would be the case with a proton-donating acid such as HCl. The cation formed in the initiation step reacts with a second monomer, forming a new cation that reacts in turn with a third monomer. As each subsequent monomer adds to the chain, the positively charged propagating site always ends up on the last unit added.

Chain initiating step

$$BF_3 + CH_2 = C$$

 $CH_3 \longrightarrow F_3 \overline{B} - CH_2 C^+$
 $CH_3 \longrightarrow CH_3$

the alkene monomer reacts with an electrophile

Chain propagating steps

$$F_{3}\overline{B}-CH_{2}C^{+}+CH_{2}=C^{C}H_{3}$$

$$F_{3}\overline{B}-CH_{2}C^{+}+CH_{2}=C^{C}H_{3}$$

$$F_{3}\overline{B}-CH_{2}CCH_{2}C^{+}+CH_{2}CH_{3}$$

$$F_{3}\overline{B}-CH_{2}CCH_{2}C^{+}+CH_{3}CH_{3}$$

$$F_{3}\overline{B}-CH_{2}CCH_{2}CH_{2}C^{+} + CH_{2}=C \xrightarrow{CH_{3}} F_{3}\overline{B}-CH_{2}CCH_{2}CCH_{2}C^{+} \xrightarrow{CH_{3}} CH_{3} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3$$

Cationic polymerization can be terminated by loss of a proton or by addition of a nucleophile that reacts with the propagating site. The chain can also be terminated by a chain-transfer reaction with the solvent (XY).

Three ways to terminate the chain

Loss of proton

$$F_{3}\overline{B} \longrightarrow CH_{2}C \longrightarrow CH_{3} \xrightarrow{CH_{3}} CH_{2}C \longrightarrow CH_{2}C \xrightarrow{CH_{3}} CH_{2}C \xrightarrow{CH_{3$$

reaction with a nucleophile

$$F_{3}\overline{B} \longrightarrow CH_{2}C \longrightarrow CH$$

chain-transfer reaction with the solvent

$$F_{3}\overline{B} \longrightarrow CH_{2}C \longrightarrow CH_{3} \begin{bmatrix} CH_{3} \\ -CH_{2}C \\ -CH_{3} \end{bmatrix} \begin{pmatrix} CH_{3} \\ -CH_{3} \\ -CH_{3} \end{bmatrix} \begin{pmatrix} CH_{3} \\ -CH_{3} \\ -CH_{3} \\ -CH_{3} \end{bmatrix} \begin{pmatrix} CH_{3} \\ -CH_{3} \\ -CH_{3$$

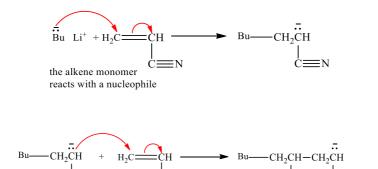
The carbocation intermediates formed during cationic polymerization, like any other carbocations, can undergo rearrangement by either a 1,2-hydride shift or a 1,2-methyl shift if rearrangement leads to a more stable carbocation. The extent of rearrangement depends on the reaction temperature. The stability order of carbocation is $3^0 > 2^0 > 1^0 > \text{methyl}$.

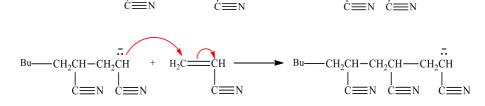
3. Anionic Polymerization

In anionic polymerization, the initiator is a nucleophile that reacts with the alkene to form a propagating site that is an anion. Nucleophilic attack on an alkene does not occur readily because alkenes are themselves electron rich. Therefore, the initiator must be a very good nucleophile, such as sodium amide or butyllithium, and the alkene must contain an electron-withdrawing substituent to decrease its electron density.

chain-initiating step

chain-propagating steps

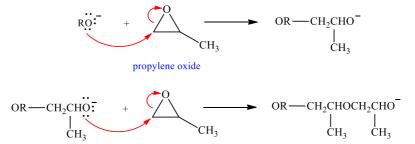




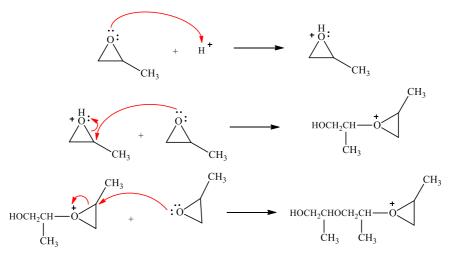
The chain can be terminated by a chain transfer reaction with the solvent or by reaction with an impurity in the reaction mixture. If the solvent cannot donate a proton to terminate the chain and if all impurities that can react with a carbanion are rigorously excluded, chain propagation will continue until all the monomer has been consumed. At this point, the propagating site will still be active, so the polymerization reaction will continue if more monomer is added to the system. Such nonterminated chains are called **living polymers** because the chains remain active until they are "killed." Living polymers usually result from anionic polymerization because the chains cannot be terminated by proton loss from the polymer, as they can in cationic polymerization, or by disproportionation or radical recombination, as they can in radical polymerization.

Ring-Opening Polymerizations

Although ethylene and substituted ethylenes are the monomers most commonly used for chain-growth polymerization reactions, other compounds can polymerize as well. For example, epoxides undergo chain-growth polymerization reactions. If the initiator is a nucleophile such as OH⁻ or RO⁻ polymerization occurs by an anionic mechanism.



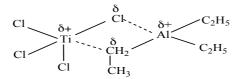
If the initiator is a Lewis acid or a proton- donating acid, epoxides are polymerized by a cationic mechanism. Polymerization reactions that involve ring-opening reactions, such as the polymerization of propylene oxide, are called **ring-opening polymerizations**.



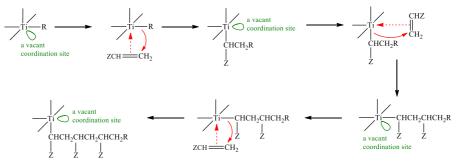
4.4. ZIEGLER-NATTA POLYMERISATION

An efficient and stereospecific catalytic polymerization procedure was developed by Karl Ziegler (Germany) and Giulio Natta (Italy) in the 1950's. Their findings permitted, for the first time, the synthesis of unbranched, high molecular weight polyethylene (HDPE), laboratory synthesis of natural rubber from isoprene, and configurational control of polymers from terminal alkenes like propene (e.g. pure isotactic and syndiotactic polymers). In the case of ethylene, rapid polymerization occurred at atmospheric pressure and moderate to low temperature, giving a stronger (more crystalline) product (HDPE) than that from radical polymerization (LDPE). For this important discovery these chemists received the 1963 Nobel Prize in chemistry.

Ziegler-Natta catalysts $[(C_2H_5)_3Al + TiCl_4]$ are prepared by reacting certain transition metal halides with organometallic reagents such as alkyl aluminum, lithium and zinc reagents. The catalyst formed by reaction of triethylaluminum with titanium tetrachloride has been widely studied, but other metals (e.g. V & Zr) have also proven effective. The structure of this catalyst is as follows:



The following diagram presents one mechanism for this useful reaction. Others have been suggested, with changes to accommodate the heterogeneity or homogeneity of the catalyst. Polymerization of propylene through action of the titanium catalyst gives an isotactic product; whereas, vanadium based catalyst gives a syndiotactic product.



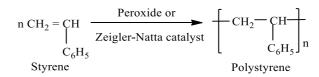
The mechanism of the Ziegler–Natta catalyzed polymerization of a substituted ethylene. A monomer forms a π complex with an open coordination site of titanium and then is inserted between the titanium and the growing polymer.

4.5. SYNTHESIS, PROPERTIES AND USES OF COMMERCIAL ADDITION POLYMERS

Following are the some of the important polymers and their uses.

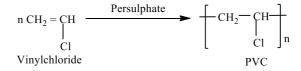
4.5.1. Polystyrene or Styrene

Polystyrene can be prepared either by free radical polymerization or by Zeigler-Natta polymerization. Free radical polymerization gives atactic polymer whereas Zeigler-Natta polymerization gives isotactic polymer. It is a good light weight material and is used for making plastic toys, household wares, telephone, radio and television bodies and refrigerator lining. It is also used as high frequency insulator.



4.5.2. Polyvinyl chloride (PVC)

It is prepared by free radical polymerization in the presence of persulphate as an initiator.



It is pliable (easily moulded) polymer and thus has very wide range of applications. It is used for making raincoats, hand bags, plastic toys, shoe soles and vinyl flooring. It is good electrical insulator.

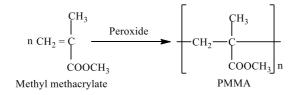
4.5.3. Polythene

Two types of polythene are commercially produced; a high density polythene (HDPE) and a low density polythene (LDPE).

High Density Polythene (HDPE)	Low Density Polythene (LDPE)	
 n CH₂=CH₂ 333-343 K 6-7 atm TiCl₄ + Al(C₂H₅)₃ Polythene It consists of linear chain polymers molecule. Density is 0.97 g cm⁻³ Melting point 403 K It is transluscent polymer. It is chemically inert, having relatively greater toughness and high tensile strength than LDP. Used in manufacture of containers, pipes, bottles, toys, bags,etc. 	 n CH₂=CH₂ 350-570 K 1000-1500 atm Trace O₂ Polythene It consists of branched chain structure of polymer molecules. Density is 0.92 g cm⁻³ Melting point 383 K It is transparent polymer. It is also chemically inert with moderate tensile strength and high toughness. Used as packing material in the form of thin film or sheet, also as 	
	insulation for electrical wires and cables.	

4.5.4. Polymethyl methacrylate (PMMA)

Monomer of PMMA is methyl methacrylate. It is prepared by free radical polymerization in the presence of peroxide.



The polymer is sold under various trade name, viz., plexiglass, Lucite, and crystallite. It is a transparent and colourless plastic. It is used as a substitute for glass because it is water white and over 90% transparent. It is use to make safety glass in automobile, wind-shields and transparent pipes and tubings as well as plexiglass. It is also used for contact lenes, TV screen and in skylight. It is also used in fibres.

4.5.5. Polyacrylonitrile (PAN)

It is prepared by free radical polymerization of vinylcyanide in the presence of H₂SO₄/ FeSO₄.

n CH₂ = CH
$$\xrightarrow{H_2O_2/\text{FeSO}_4}$$
 $\xrightarrow{(CH_2 - CH_1)_n}$
CN $\xrightarrow{(CH_2 - CH_2)_n}$ Polyacrylonitrile

Polyacrylonitrile is hard, horny and highly crystalline polymer. It is a major constituent of acrylic fibres, viz., **Orlon** (commercial name). It is mainly used in artificial wool.

4.5.6. Teflon

Teflon is the brand name for a number of fluorinated vinyl polymers. The most important Teflon is polytetrafluroethylene (PTFE). It is prepared by free radical polymerization of tetrafluroethylene in the presence of ammonium peroxosulphate at high temperature under high pressure.

n CF₂ = CF₂
$$\xrightarrow{(NH_4)_2S_2O_8}$$
 $\xrightarrow{(F_2-CF_2)_n}$

It is a white solid mp. 600 K and is a tough flexible material. It has exceptional resistance to chemicals and is inert towards all type of reagents except molten alkali metals and fluorine (It is inert even to boiling aqua regia). It has high thermal stability (upto 360° C) and retains its properties over a wide temperature range. The polymer may be used upto 300° C for long periods. Because of its great chemical inertness and highly thermal stability, Teflon is used for making non-stick utensils.

E-Content: Polymers

Teflon is good electrical insulator. Thus, Teflon is used in two main fields namely chemical and electrical applications. Electrical applications include wire coating, holders and spacers for use in aggressive conditions. A chemical application includes gaskets, pump parts and laboratory equipments.

4.6. STEP-GROWTH POLYMERS

Step-growth polymers are formed by the intermolecular reaction of bifunctional molecules (molecules with two functional groups). When the functional groups react, in most cases a small molecule such as water, alcohol, or HCl is lost. This is why these polymers are also called *condensation polymers*. There are two types of step-growth polymers. One type is formed by the reaction of a single monomer that possesses two different functional groups A and B. Functional group A of one monomer reacts with functional group B of another monomer.

А—В А—В — → A—X—B

The other type of step-growth polymer is formed by the reaction of two different bifunctional monomers. One monomer contains two A functional groups and the other monomer contains two B functional groups.

► A—X—B

в—в –

4.7. COMMERCIAL CONDENSATION POLYMERS

Condensation polymers can be classified into the following groups

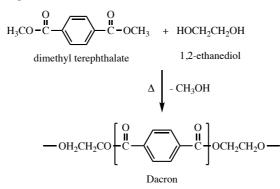
4.7.1. Polyesters

Polyesters are defined as polymers contain recurring -COO- group in the main chain.

A—A

1. Polyethylene Terephthalate (PET) or Dacron or Mylar

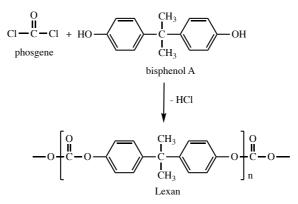
The monomers of PET are terephthalic acid and ethylene glycol. In practice PET is prepared from dimethyl ester of terephthalic acid and ethylene glycol. The reaction is given below:



It is a linear polymer having high tensile strength, high modules, good elongation, good thermal stability and spin ability. It is extensively used to make textile fibers due to the above properties. Garments made from its fibers resist the formation of wrinkles and are easy to wash. Moreover, terylene fibers are blended with other fibers such as wool and cotton to produce "wash and wear" fabrics. It is also used in seat belts and sails. It is also used in mylar in the preparation of firms, magnetic recording tapes and for packing frozen food.

2. Lexan

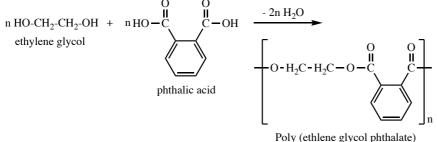
Polyesters with two ester groups bonded to the same carbon are known as **polycarbonates**. Lexan is produced by the reaction of phosgene with bisphenol A. Lexan is a strong, transparent polymer used for bulletproof windows and traffic-light lenses. In recent years, polycarbonates have become important polymers in the automobile industry as well as in the manufacture of compact discs.



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3. Glyptal or Alkyd Resin

Glyptal is a general name of all polymers obtained by condensation of di-basic acids, and polyhydric alcohols. The simplest glyptal is poly (ethylene glycol phthalate) which is obtained by the condensation of ethylene glycol and phthalic



acid.

Uses: It is a thermoplastic. It dissolves in suitable solvents and the solution on evaporation leaves a tough but not flexible film. It is therefore, used in the manufacture of paints and lacquers.

4.7.2. Polyamides

Polyamides are defined as polymers which contain repeating amide group (-CONH-) in the main polymer chain.

1. Nylon-6,6

It is manufactured by the condensation polymerization of adipic acid and hexamethylene diamine at 525 K under pressure.

$$n \operatorname{NH}_2(\operatorname{CH}_2)_6\operatorname{NH}_2 + n \operatorname{HOOC}(\operatorname{CH}_2)_4\operatorname{COOH} \xrightarrow{-n \operatorname{H}_2\operatorname{O}} \left[\operatorname{NH}(\operatorname{CH}_2)_6\operatorname{NHCO}(\operatorname{CH}_2)_4\operatorname{CO}\right]_n$$

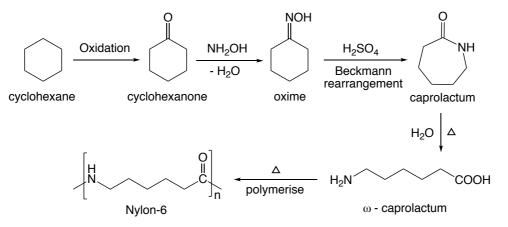
Nylon 6, 6

It is called nylone 6,6 since both adipic acid and hexamethylene diamine contains six carbons each. Generally, condensation reactions are irreversible, but nylone 6,6 is an exception.

Uses: It is a linear polymer. Nylone 6,6 fibers have high tensile strength, are tough, abrasion resistant and somewhat elastic, nylon 6,6, therefore, used in the manufacture of carpets, textile fibers and bristles. Crinkled nylon fibers are used for making elastic hosiery.

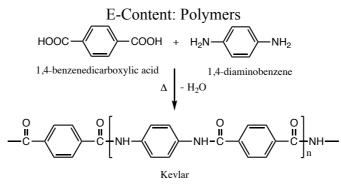
2. Nylon-6 or Perlon

It is obtained from the monomer caprolactum. Caprolactum is obtained from cyclohexane according to the reaction sequence given below:



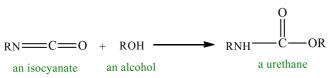
Nylon-6 is used for manufacture of tyre cards, fabrics and ropes.

3. One super fiber is **Kevlar**, a polymer of 1,4-benzenedicarboxylic acid and 1,4-diaminobenzene. The incorporation of aromatic rings into polymers has been found to result in polymers with great physical strength. Aromatic polyamides are called **aramides**. Kevlar is an aramide with a tensile strength greater than that of steel. Army helmets are made of Kevlar, which is also used for lightweight bulletproof vests and high-performance skis. Because it is stable at very high temperatures, it is used in the protective clothing worn by firefighters.

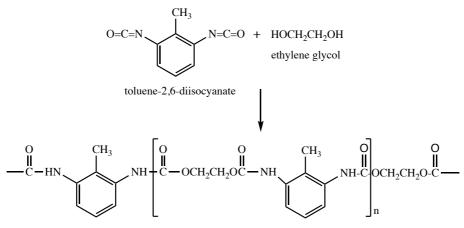


4.7.3. Polyurethanes

A **urethane**—also called a carbamate—is a compound that has an OR group and an NHR group bonded to the same carbonyl carbon. Urethanes can be prepared by treating an isocyanate with an alcohol.



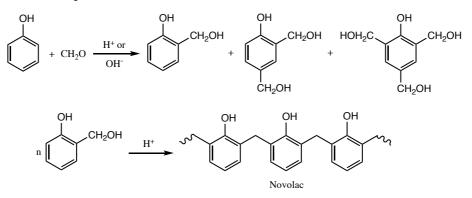
Polyurethanes are polymers that contain urethane groups. One of the most common polyurethanes is prepared by the polymerization of toluene-2,6-diisocyanate and ethylene glycol. If the reaction is carried out in the presence of a blowing agent, the product is a polyurethane foam. Blowing agents are gases such as nitrogen or carbon dioxide. At one time, chlorofluorocarbons—low-boiling liquids that vaporize on heating—were used, but they have been banned for environmental reasons. Polyurethane foams are used for furniture stuffing, carpet backings, and insulation. Notice that polyurethanes prepared from diisocyanates and diols are the only step-growth polymers that we have seen in which a small molecule is *not* lost during polymerization.



Polyurethane

One of the most important uses of polyurethanes is in fabrics with elastic properties, such as spandex (Lycra). These materials are block copolymers in which some of the polymer segments are polyurethanes, some are polyesters, and some are polyamides. The blocks of polyurethane are soft, amorphous segments that become crystalline on stretching. When the tension is released, they revert to the amorphous state.

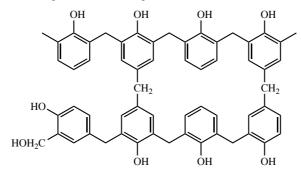
4.7.4. Phenol-Formaldehyde Resins



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These are made by the reaction of phenol and formaldehyde in basic medium. The reaction involves of formation of methylene bridges in ortho, para or ortho as well as para position. Bakelite is a cross-linked thermosetting polymer. Soft bakelites with low degree of polymerization are used as bonding glue for laminated wooden planks, in the preparation of varnishes and lacquers. High degree of polymerization leads to formation of hard bakelite which is used for making combs, fountain pen barrels, gramophone records, electrical goods, formica table tops and many other products. Sulphonated bakelites are used as ion-exchange resins for softening of hard water. The reaction starts with the initial formation of o-and/ or p-hydroxymethylphenol derivatives, which further react with phenol to form compounds having rings joined to each other through - CH₂ groups. The initial product could be a linear product - Novolac used in paints.

Novolac on heating with formaldehyde undergoes cross linking to form infusible solid mass called bakelite.



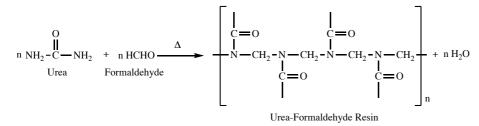
Cross-link phenolic resin (Bakelite)

Phenol resins are rigid, hard, scratch resistant, infusible, water resistant, insoluble solid, resistant to non-oxidizing agent but are attacked by alkalis. They have good electrical insulating character.

Bakelite is used in making electric insulating parts like switches, plugs, switch boards etc, making molded articles like telephone parts, cabinets for radio and TV, an adhesives for grinding wheels, in paints and varnishes.

4.7.5. Urea-Formaldehyde Resins

Urea-formaldehyde is chemically known as the urea-methanal .It is a non-transparent thermo setting resin or plastic and is made from urea and formaldehyde heated in the presence of a mild base such as ammonia or pyridine. It is first time synthesized in 1884 by Hölzer, with coworker Bernhard Tollens. In 1919, Hanns John (1891–1942) of Prague, Czechoslovakia obtained the first patent for urea formaldehyde resin.

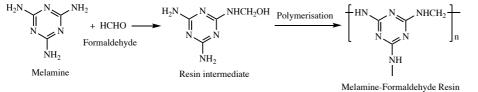


Urea formaldehyde is the very common chemical and is mostly used because of its chemical properties. Examples are textiles, paper, foundry sand molds, wrinkle resistant fabrics, cotton blends, rayon, corduroy, etc. also used to glue wood together. Urea formaldehyde is mostly used when producing electrical appliances casing also desk lamps. It is widely chosen as an adhesive because of its property of high reactivity.

Urea formaldehyde is also used in agricultural field as a source of nitrogen fertilizer and Its rate of decomposition is into CO_2 and NH_3 and is determined by the action of microbes found naturally in soils.

4.7.6. Melamine-Formaldehyde Resins

Melamine formaldehyde polymer is formed by the condensation polymerisation of melamine and formaldehyde.



It is used in the manufacture of unbreakable crockery.

E-Content: Polymers

4.8. NATURAL RUBBER

Rubber is a natural polymer and possesses elastic properties. It is also termed as elastomer and has a variety of uses. It is manufactured from rubber latex which is a colloidal dispersion of rubber in water. This latex is obtained from the bark of rubber tree and is found in India, Srilanka, Indonesia, Malaysia and South America. Natural rubber may be considered as a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as cis - 1, 4 - polyisoprene.

$$\begin{array}{ccc} CH_3 & CH_3 & CH_3 \\ I & I & I \\ \sim H_2C - C = CH - CH_2 - CH_2 - C = CH - CH_2 - CH_2 - C = CH - CH_2 \wedge CH_2 - CH_2 - CH_2 - CH_2 - CH_2 \wedge CH_2 + CH_2 + CH_2 \wedge CH_2 + C$$

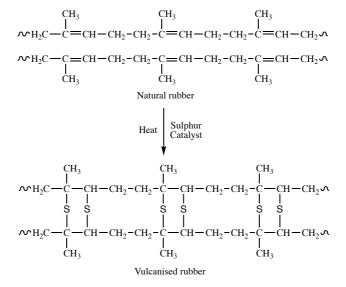
The cis-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure. Thus, it can be stretched like a spring and exhibits elastic properties.

$$H_{2}C = C - CH = CH_{2}$$

Isoprene

4.9. VULCANISATION OF RUBBER

Natural rubber becomes soft at high temperature (>335 K) and brittle at low temperatures (On vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened. In the manufacture of tyre rubber, 5% of sulphur is used as a crosslinking agent. The probable structures of vulcanised rubber molecules are depicted below:



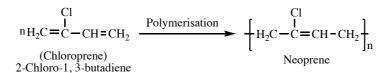
4.10. SYNTHETIC RUBBERS

Synthetic rubber is any vulcanisable rubber like polymer, which is capable of getting stretched to twice its length. However, it returns to its original shape and size as soon as the external stretching force is released. Thus, synthetic rubbers are either homopolymers of 1, 3 - butadiene derivatives or copolymers of 1, 3 - butadiene or its derivatives with another unsaturated monomer.

4.11. PREPARATION OF SYNTHETIC RUBBERS

4.11.1. Neoprene

Neoprene or polychloroprene is formed by the free radical polymerisation of chloroprene.



It has superior resistance to vegetable and mineral oils. It is used for manufacturing conveyor belts, gaskets and hoses.

4.11.2. Buna – N or Nitrile Rubber or NBR

Buna –N is obtained by the copolymerization of 1, 3– butadiene and acrylonitrile in the presence of a peroxide catalyst. The mixture of 1, 3– butadiene and acrylonitrile should be present in 3:1 ratio.

n H₂C=CH-CH=CH₂ + n H₂C=CH
1,3-Butadiene Acrylonitrile Polymerisation
$$+$$
 H₂C-CH=CH-CH₂-CH₂-CH
Buna-N

Nitrile rubber (GR-A) has low swelling, low solubility, good tensile strength and abrasion resistance even after immersion in gasoline or oils. It has good heat resistance. It is used in fuel tanks, gasoline houses, as an adhesive and in the form of latex.

4.11.3. Buna – S or Styrene Rubber or SBR

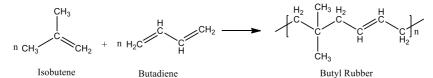
Buna -S is obtained by the copolymerization of 75% 1, 3- butadiene and 25% styrene in the presence of a peroxide catalyst.

$$n H_2C = CH - CH = CH_2 + n H_2C = CH_1 \xrightarrow{C_6H_5} Polymerisation + H_2C - CH = CH - CH_2 - CH_2 - CH_1 + H_2C - CH_2 - CH_2 + H_2C +$$

It is a vulcanized by sulphur. It is very tough and is good substitute for natural rubber. It possesses high abrasion resistance, high load bearing capacity, low oxidation resistance, swells in oil and organic solvents. SBR used in motor tyres, shoes soles, foot wear components, insulation of wire and cables, gaskets adhesives, etc.

4.11.4. Butyl Rubber

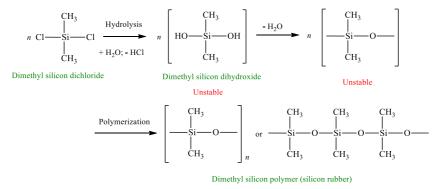
It is a copolymer of 98% isobutene and 2% butadiene. The butadiene is added to introduce the necessary ethylenic linkage for vulcanization.



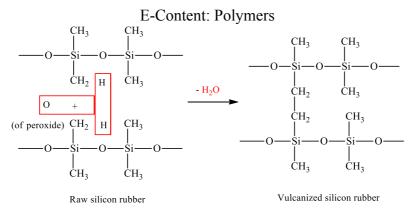
Butyl rubber is amorphous under normal conditions but gets crystallized on stretching. It has excellent resistance to heat, abrasion, ageing, chemicals (such as H_2SO_4 , HNO_3 , HCl or HF), polar solvents but is soluble in non- polar solvents like benzene. It is used in manufacture of inner tubes for automobile tyres. It is used for wire insulation.

4.12. SILICON RUBBER

Silicone rubber is an elastomer (rubber-like material) composed of silicone—itself a polymer—containing silicon together with carbon, hydrogen, and oxygen. Silicon rubber is produced by the polymerization of dimethyl silicon hydroxide.



Due to the unsaturated character, the polymer can be vulcanized by organic peroxide to form cross links between two adjacent chains.



Silicone rubber is generally non-reactive, stable, and resistant to extreme environments and temperatures from -55 °C to +300 °C while still maintaining its useful properties. Silicone rubbers are widely used in industry including automotive applications; cooking, baking, food storage products; apparel such as undergarments, sportswear, footwear; electronics and medical devices.

4.13. MOLECULAR WEIGHT OF POLYMERS

Two types of average molecular weights have been defined.

1. Number average molecular weight

$$\overline{M_n} = \frac{\sum n_i M_i}{\sum n_i}$$

where $n_i M_i$ stands for the weight of macromolecules numbering n_i and having molecular weight M_i

2. Weight average molecular weight

$$\overline{M}_{w} = \frac{\sum n_{i} M_{i}^{2}}{\sum n_{i} M_{i}}$$

These two molecular weights are compared as follows

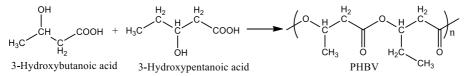
$$M_w > \overline{M_n}$$

4.14. BIODEGRADABLE POLYMERS

A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric solid waste materials. These solid wastes cause acute environmental problems and remain undegraded for quite a long time. In view of the general awareness and concern for the problems created by the polymeric solid wastes, certain new biodegradable synthetic polymers have been designed and developed. These polymers contain functional groups similar to the functional groups present in biopolymers. Aliphatic polyesters are one of the important classes of biodegradable polymers. Some important examples are given below:

4.14.1. Poly β -hydroxybutyrate – co- β -hydroxy valerate (PHBV)

It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3 – hydroxypentanoic acid. PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.



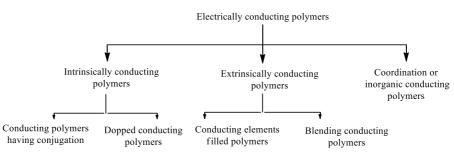
4.14.2. Nylon 2–nylon 6

It is an alternating polyamide copolymer of glycine (H_2N - CH_2 -COOH) and amino caproic acid [H_2N (CH_2)₅ COOH] and is biodegradable.

n H₂N-CH₂-COOH + n H₂N (CH₂)₅ COOH
$$\rightarrow$$
 (HN-CH₂-C-HN (CH₂)₅ C)
Glycine Amino caproic acid Nylon 2-nylon 6

4.15. CONDUCTING POLYMERS

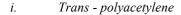
"Polymer which can conduct electricity are called electrically conducting polymers or simply called conducting polymers". Ordinary polymers obtained by usual methods are electrically insulator. However some specific polymers may act as conductors. These polymeric conductors possess electrical conductivity on par with metallic conductors. Conductivities as high as 1.5×10^7 Ohm⁻¹ m⁻¹ have been attained in these polymeric materials. Such polymers are useful because of their ease of fabrication, flexibility or strength, lightness of weight and chemical inertness. Since many metals are heavy and are prone to corrosion, metalloid semiconductor are brittle and are exceedingly difficult to purify and fabricate, polymers that conduct electricity have become very important and have a wide variety of uses. It ranges from easily fabricated semiconductor chips and integrated circuits to electrodes, light weight battery components, sensors etc. This is the reasons why the conducting polymers have become very important today. Electrically conducting polymers can be classified into the following groups:

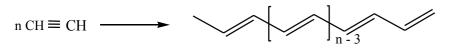


4.15.1. Intrinsically conducting polymers

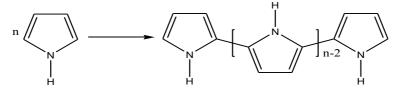
This type of polymers has a solid backbone made up of extensive conjugated system, which is responsible for conductance. Depending upon the constituents of backbone, they may again be of two types:

1. Conjugated polymers having conjugated pi electrons in the backbone: Such types of polymers essentially contain conjugated pi electrons backbone. These pi electrons are loosely held electrons and are responsible for electrical charge. Under the influence of electric field conjugated pi electrons of the polymer get excited, which can then be transported through the solid polymers. Overlapping of orbitals of conjugated pi electrons over the entire backbone results in the formation of valence bond as well as conduction bonds, which extend over the complete polymer molecule. Thus presence of conjugated pi electron in a polymer increases its conductivity to a large extent. Important commercially produced conducting polymers are:





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ii. Poly-pyrrole
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2. Dopped Conducting Polymers

The conducting polymers obtained by exposing the polymer (generally intrinsically conducting polymers, ICP, having conjugated pi electrons) to a charge transfer agent in either gas phase or in solution are called doped conducting polymers. Doping is the process by which conductivity of the polymers may be increased by creating negative or positive charge on the polymer backbone by oxidation or reduction.

Intrinsically conducting polymers, such as polyacetylene, possess low conductivity, low ionization potential and high electron affinity. Hence these polymers can be dopped with electron donors such as alkali metals or electron acceptors such as Lewis acids. Thus dopping is of two types:

p- Doping: p- dopping is a technique in which an ICP is oxidized with Lewis acid (which is a electron acceptor) creating the positive charge on the backbone of the polymer. Some of the common p- dopant are I₂, Br₂, FeX₃, PF₅, AsF₅, etc.

E-Content: Polymers

$$(C_{2}H_{2})n + 2FeCl_{3} \longrightarrow (C_{2}H_{2})n^{+} FeCl_{4}^{-} + 2FeCl_{2}$$
(Oxidation)
$$2(C_{2}H_{2})n + 3I_{2} \longrightarrow 2[(C_{2}H_{2})^{+} I_{3}^{-}$$
(Oxidation)

i. n- Dopping: This is a technique in which ICP is reduced with Lewis bases creating the negative charge on the backbone of the polymer. Some of the common n-dopant used are Li, Na, K, Ca, etc.

 $(C_2H_2)_n + Na \longrightarrow (C_2H_2)^- Na^+$

4.15.2. Extrinsically conducting polymers (ECP)

This type of polymers own their conductivity due to the presence of externally added ingredients in them. It is of two types.

i. Conductive element filled polymers: In this, the polymers act as the binder to hold the conducting material (such as carbon black, metallic fibers, metallic oxides etc.) together in the solid entity.

Minimum concentration of conductive filler which should be added so that polymer starts conducting is known as percolation threshold. Carbon black is very useful as filter. These polymers bear good conductive properties and low in cast, light in weight, as well as durable.

ii. Blended conducting polymers: It is obtained by blending a conventional polymer with a conducting polymer. Such polymers possess better physical, chemical, electrical and mechanical properties and they can be easily processed.

4.15.3. Co-ordination or Inorganic co-ordination polymers

These polymers contain charge transfer complexes and are obtained by combining metal with polydentate ligands. Such polymers have very low degree of polymerization.

4.15.4. Applications

- i. In rechargeable light weight batteries.
- ii. Used in making button type batteries.
- iii. Used in conductive paints.
- iv. Used as electrochemical accumulators.
- v. Used as biosensors and chemical sensors.
- vi. Used in optical display devices.
- vii. Used in solar cells.
- viii. Used in photovoltaic system.
- ix. Used in electric devices.
- x. Used in telecommunication systems.
- xi. Used in smart windows.

4.16. COMPOSITES

Composites are those materials which are made up of more than one component. Polymers belonging to different classes posses different properties. So as to enhance its properties, the polymers may be mixed with some other polymers or non-polymeric materials.

Most of the composite materials are composed of two phases one is termed a matrix which is continuous and surrounds the other phase often called the dispersed or reinforced phase. The reinforcing material and the matrix can be metal, ceramic or polymer. Reinforcing materials are strong with low density while the matrix is usually a ductile or tough material.

4.17. MATERIALS USED IN POLYMER COMPOSITES

Composites are usually made up of two components, a fibre and a matrix. The fibre is most often glass, carbon fibre, polyethylene or polydicyclopentadiene.

The materials used for:

Fibre: Glass fibre, carbon fibre and aramid.

Resin: Thermosetting: Polyester epoxides

Thermoplastic: Polyolefins, polyimides, vinylic polymers, polyacetals, polycarbonate and polyphenylene.

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Additives: For structural application, it is necessary to achieve some degree of flame retundance. Flame retardant additives are mixed in the resin itself. Fillers and pigments are also used in the process.

4.18. CLASSIFICATION

Polymer matrix composites are classified as

4.18.1. Conductive composites

These conductive composites are based on polymers which conduct the charge at molecular level. They contain the backbone or pendent groups which are responsible for the generation and propagation of charge carries. Thus conductivity can be varied by controlling the extant of oxidation or reduction.

These composites are mostly used for electrostatic discharge (ESD) and electromagnetic shielding (EMIS) of sophisticated electronic devices including computer.

4.18.2. Non-conductive composites

Non-conducting composites are prepared by using polymer matrix like PPG styrene, acrylonitrile (SAN) and spereoidal fillers. These composites have increased modulus of elasticity and strength but the fillers decrease the impact strength. To avoid this defect the polymer matrix is first modified with coupling agents and then mixed with fillers. PP is modified with polybutadiene rubber (PBR) and then mixed with mica. The composites thus obtained have improved tensile and flexural strengths heat distortion temperature and impact strength.

4.18.3. High performance in-situ composites

The composites from liquid crystals are a highly technical process. Polymer liquid crystals when properly blended with engineering and special plastics give composites with increased modulus and strength. The permeability and thermal expansion decreases. Such blends are known as in-situ composites. Vectra polymer liquid crystals on being blended with polyethylene ether-ketone (PEEK) improve the mechanical properties of PEEK. Nylon 6 on being blended with PEEK gives increased modulus.

4.18.4. Carbon fibre based composites

The composites of thermoplastic matrix and carbon fibre are processed by twin crew extruders.

4.18.5. Heat resistance composites

Composites of glass fibre and polyamide inside matrix are heat resistant. Polyamide inside when blended with epoxy resins gives better heat resistance upto 250° C.

4.18.6. Cement polymer composites

Both polar and non-polar materials are mixed with free mortar matrix and then the monomer is incorporated. The compressive and tensile strength of the cement composite is very much increased and they are more durable especially in saline water.

4.19. ORGANOMETALLIC COMPOUNDS

Organic compounds that contain carbon metal bonds are called organometallic compounds. Organometallic compounds are mainly classified into two types:

- 1. Sigma (σ) bonded organometallic compounds
- 2. Pi (π) bonded organometallic compounds

4.19.1. Sigma (σ) bonded organometallic compounds

General structure of sigma bonded organometallic compounds is represented by R-M. The bond between R and M is sigma bonded. The nature of carbon metal bond mainly depends on electropositive character of the metal. More is the electropositive character of the metal, more is the ionic character between carbon – metal bond and more is reactivity of organometallic compound.

In organometallic compounds carbon is bonded with electropositive atom hence carbon bears negative charge and metal bears positive charge. Thus organic part R of R-M behaves as a nucleophile as well as a base. More is electropositive character of M, more is the nucleophilicity and basicity of R of R-M. These organometallic compounds are named by writing the name of the meal after organic group. Some examples are:

R-Li	Alkyl lithium
C ₂ H ₅ -Li	Ethyl lithium
C ₆ H ₅ -Li	Phenyl lithium
R-Mg-Cl	Alkyl magnesium halide
CH ₃ -Mg-Cl	Methyl magnesium halide
C ₆ H ₅ -Mg-Cl	Phenylmagnesium halide
$CH_2 = CH-CH_2-I$	Allyl magnesium iodide
R-Zn-R	Dialkyl zinc
C_2H_5 -Zn- C_2H_5	Diethyl zinc
$(C_2H_5)_4Pb$	Tetraethyl lead

Preparation

From metal and halides. When metal is treated with halides in the presence of suitable solvent, generally ether and inert atmosphere, organometallic compound is formed.

 $R-X + Mg \xrightarrow{\text{Ether}} RMgX$ $R-X + 2Li \xrightarrow{\text{Ether}} R-Li + LiX$

From RMgX or RLi : RMgX or RLi reacts with inorganic halides to form other organometallic compounds.

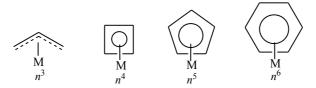
 $3CH_{3}MgBr + BCl_{3} \longrightarrow (CH_{3})_{3}B + 3Mg(Cl)Br$ $3CH_{3}MgBr + AlCl_{3} \longrightarrow (CH_{3})_{3}Al + 3Mg(Cl)Br$

4.19.2. Pi (π) bonded organometallic compounds

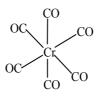
Pi-bonded organometallics are formed between a metal atom (transition metal atom, ion or complex species) and ligands having at least one pi bond. In such compounds the metal atom is bonded to the ligands, in such a way that the donation of electrons and the back acceptance by the ligand is possible by the use of pi orbitals of the ligands and d orbitals of the metal.

In order to name pi complexes the number of carbon atoms which are bonded to the metal atom are indicated by the Greek letter, η (eta). It is then followed by a number as η^2 , η^3 , η^4 etc. η^5 means five carbon atoms are bonded to the central atoms. For example, Fe($\eta^5 - C_5H_5$)₂ is *bis* (cyclopentadienyl) iron.

In a large number of pi bonded transition metal organometallic compounds generally the entire unsaturated hydrocarbon molecule is involved in the electron donation with no preferential bonding between the metal atom and any single carbon atom of the organic molecules.



However, a significant number of examples are known in which preferential bonding sites have been stablished. Another type of ligands which form pi bonded organometallics are carbon monoxide, carbine, benzyne etc. In these derivatives only one carbon atom of the ligand is within the bonding distance of the metal.



Preparation

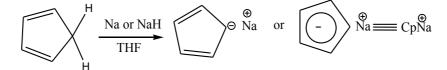
From ligands and metal halide or metal carbonyl: The olefin complexes can be obtained treating metal halide or a metal carbonyl with a ligand.

$$H_{2}C = CH - CH = CH_{2} + Fe(CO)_{5} \xrightarrow{\Delta} C_{4}H_{6}Fe(CO)_{3} + 2CO$$

$$H_{2}C = CH_{2} + K_{2}[PtCl_{4}] \xrightarrow{\text{Potassium}} K[(C_{2}H_{4})PtCl_{3})] + KCl$$

$$Zeise's salt$$

Preparation of π -cyclopentadienyl metal complexes: Alkali metal react with cyclopentadiene to give cyclopentadienyl anion.



Cyclopentadienyl anion reacts with metal salts to form metallocenes :

$$MCl_2 + 2CpNa^+ \longrightarrow MCp_2 + 2NaCl$$

Arene -metal complexes : Arene metal complexes can be prepared by reacting the vapours of the metal with hydrocarbon.

$$2C_6H_6 + Cr (vapours) \longrightarrow [Cr(C_6H_6)_2]$$

Dibenzene chromium

4.20. GRIGNARD REAGENTS

The organomagnesium halides are known as **Grignard reagents**. These are extremely important reagents developed by the French chemist François Auguste Victor Grignard, who was awarded the Nobel Prize in 1912 in Chemistry for this work. The Grignard reagent is represented as **R-Mg-X**, where

$$\label{eq:result} \begin{split} R &= alkyl \ / \ aryl \ / \ alkenyl \ / \ allyl \ group \\ X &= Cl \ / \ Br \ / \ I \end{split}$$

4.21. PREPARATION OF GRIGNARD REAGENTS

The Grignard reagents are prepared by the action of activated magnesium (Rieke magnesium) on organic halides in suitable solvents like Diethyl ether, Et₂O or Tetrahydrofuran, THF in *anhydrous conditions*.

$$\delta^+ \delta^-$$
 Anhydrous $\delta^- \delta^+$
R-X + Mg \longrightarrow Et₂O (or) THF

This is an oxidative insertion of magnesium between carbon and halogen bond, which involves *oxidation of Mg(0) to Mg(II)*. The mechanism of this reaction if not quiet conclusive.

The Grignard reagents are in equilibrium with the dialkylmagnesium species R₂Mg and MgX₂ (Schlenk equilibrium).

$$2RMgX \longrightarrow \begin{array}{c} R - Mg - X \\ R - Mg - X \end{array} \xrightarrow{R_2Mg} R_2Mg + MgX_2$$

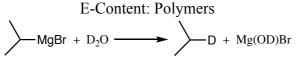
In the formation of Grignard reagent, the polarity of carbon attached to the halide group is reversed. This reversal in polarity is called as *umpolung*.

4.22. REACTIONS OF GRIGNARD REAGENTS

The Grignard reagents are highly basic and can react with protic compounds like water, acids, alcohols, 1-alkynes etc., by giving corresponding alkanes. E.g. Ethylmagnesium bromide liberates ethane gas when treated with water.

 $C_2H_5MgBr + H_2O \longrightarrow C_2H_6 + Mg(OH)Br$

The reaction of Grignard reagent with D₂O can be used to introduce a deuterium atom selectively at a particular carbon atom.



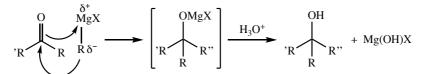
However the Grignard reagents are less basic than organolithiums and hence are more suitable nucleophiles for carbon-carbon bond formation.

The Grignard reagents are used as sources of carbon nucleophiles (carbanions) and can react with electrophilic centers. The addition reactions involving Grignard reagents with compounds containing polarized multiple bonds like aldehydes, ketones, esters, acid halides, nitriles, carbon dioxide etc., are termed as Grignard reactions.

The reactivity of carbonyl compounds with Grignard reagents follow the order: aldehydes > ketones > esters > amides

4.23. MECHANISM OF GRIGNARD REAGENTS

The first step in the Grignard reaction is the nucleophilic addition of Grignard reagent to the polar multiple bond to give an adduct which upon hydrolytic workup gives the final product like alcohol. The mechanism of reaction with a carbonyl compound is shown below.



4.24. APPLICATIONS OF GRIGNARD REAGENTS

Following is the summary chart of applications of Grignard reagent in modern organic synthesis.

Grignard reaction			Product
Aldehyde (R'-CHO)Ketone (R'-CO-R")Ester (R'-COOR")Acid halide (R'-COX)CO2CS2SO2SO3nitriles (R'-CN)	Formaldehyde (HCHO)	\rightarrow	A primary alcohol: R-CH ₂ -OH
	Aldehyde (R'-CHO)	\rightarrow	A secondary alcohol: R'-CH(OH)-R
	Ketone (R'-CO-R")	\uparrow	A tertiary alcohol: R'-CR"(OH)-R
	Ester (R'-COOR")	\rightarrow	A tertiary alcohol: R'-CR(OH)-R
	Acid halide (R'-COX)	\rightarrow	A tertiary alcohol: R'-CR(OH)-R
	CO ₂	\rightarrow	A carboxylic acid: R-COOH
	CS_2	\rightarrow	A dithionic acid: R-CSSH
	SO ₂	\rightarrow	A sulphinic acid: R-SOOH
	SO ₃	\rightarrow	A sulphonic acid: R-SO ₂ OH
	nitriles (R'-CN)	\rightarrow	A ketone: RCOR'
	Hydrogen Cyanide (HCN)	\rightarrow	An aldehyde: RCHO
	Oxiranes (epoxides)	\rightarrow	Alcohols
		\rightarrow	A ketone
	cyanogen (NC-CN)	\rightarrow	A nitrile
	choramine (NH ₂ Cl)	\rightarrow	An amine
	Iodine	\rightarrow	Alkyl iodide
	Sulfur	\rightarrow	A thiol
	halides of B, Si, P, Sn	\rightarrow	compounds with C- hetero atom bonds
	CdCl ₂	\rightarrow	Dialkyl cadmium

4.25. APPLICATIONS OF ORGANOMETALLIC COMPOUNDS AS CATALYST IN POLYMERIZATION

Free radical polymerization of ethylene takes place at very high temperature ($300 \, {}^{0}C$) and very high pressure ($1000 \, atm$). Under this condition the resulting polymer have a highly branched backbone. This branch polymer has moderate thermal and mechanical properties with limited crystallinity. This polymer is known as low density polyethylene (LDPE).

Ziegler and Natta developed a catalyst system and polymerize alkenes to give linear polymers with high stereo -selectivity at room temperatures.

4.26. APPLICATIONS OF ORGANOMETALLIC COMPOUNDS AS CATALYST IN ORGANIC SYNTHESIS

1. Wilkinson catalyst : Wilkinson catalyst is tris (Triphenylphosphine) chlororhodium. It is an extremely efficient catalyst for the homogeneous hydrogenation of non- conjugated alkenes and alkynes.

$$CH_2 = CH_2 + H_2 \xrightarrow{Wilkinson catalyst} CH_3 - CH_3$$

2. Carbonylation and carboxylation of alkenes: Alkenes gives carbonylation with CO and H_2 in the presence of $Co_2(CO)_8$. Carboxylation of alkenes takes place with CO and H_2O .

$$R-CH = CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} R-CH_2 - CH_2 - CHO$$
$$R-CH = CH_2 + CO_2 + H_2O \xrightarrow{Co_2(CO)_8} R-CH_2 - CH_2 - COOH$$



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ABOUT THE AUTHORS

E-Content: Polymers **EXERCISE**

Short Answer Questions

- 1. Distinguish between homopolymers and copolymers. Why do polymers have an average molecular weight?
- 2. Define the terms monomers and functionality.
- 3. What are thermosetting resins?
- 4. Distinguish between thermosetting and thermoplastic resins. Classify the following as thermosetting and thermoplastic: polystyrene, polyethylene, urea-formaldehyde, bakelite, teflon and nylon.
- 5. Define homopolymers and copolymers. Which of the following are homopolymers? Nylon 6, nylon -6,6, starch, terylene.
- 6. Write a brief note on biodegradable polymers.
- 7. Explain the difference between a thermoset and thermoplastic resins.
- 8. Define condensation polymerization.
- 9. Write the drawbacks of raw rubber. Discuss the process of vulcanization of rubber.
- 10. Write a short note on conducting polymers.
- 11. What are the conditions which make the polymer conducting?
- 12. What are important properties and uses of nylon-6?
- 13. Describe in brief about conducting polymers and their applications.
- 14. Write the structure of polyisoprene. How would you cross-link the chains of polyisoprene?
- 15. How would you obtain syndiotactic and isotactic polymers from propylene?
- 16. Explain why Teflon is highly chemical resistant.
- 17. What are the monomers of Buna-S and Polystyrene.
- 18. What are biodegradable polymers? Discuss their applications.

Long Answer Questions

- 1. Discuss the thermoplastic resins. Write the synthesis and applications of polystyrene and polyvinyl chloride.
- 2. How will you prepare Bakelite and Perspex polymer?
- 3. Differentiate between addition and condensation polymers. Identify the monomers in the compound: neoprene, dacron, nylon-6,6, polytetrafluoroethylene (PTFE). Also explain conducting polymers and their applications.
- 4. What is natural rubber? Write its limitations. Discuss the vulcanization process of rubber.
- 5. Describe the preparation properties and applications of (a) Buna-S (b) Nylon- 66.
- 6. What are biopolymers? Give their uses.
- 7. Write the method of preparation of following compounds: (a) Polyacrylonitrile (b) Polytetrafluoroethylene (PTFE)
- 8. (c) Neoprene (d) Dacron
- 9. What are elastomers? Give the preparation, properties and uses of Buna-S and butyl rubber.
- 10. Discuss the general methods for the preparation of organometallic compounds? What are the applications of organometallic compounds of magnesium?
- 11. What are organometallic compounds? Give the preparation and properties of organometallic compounds of lithium.
- 12. What are various types of nanocomposite materials?
- 13. What are organometallic compounds? Discuss the mechanism of the reaction of preparation of polypropylene using Ziegler-Natta catalyst. Give the structure of stereoregular polypropylene thus obtained.
- 14. What are organometallic compounds? Give the classification and preparation of organometallics.
- 15. Explain various methods of preparation of Grignard reagent and also write it's at least five applications.