

Applications

Conducting polymers have many applications, because they are generally, lighter, more flexible, and easier to fabricate than many of the materials they seek to replace.

Some of the important uses are as follows :

1. Corrosion inhibitors
2. Compact capacitors
3. Anti-static coating for clothing
4. Electromagnetic shielding for computers
5. 'Smart windows'.
6. Transistors.
7. Light emitting diodes (LEDs) based on polythiophene.
8. Lasers used in flat televisions.
9. Solar cells.

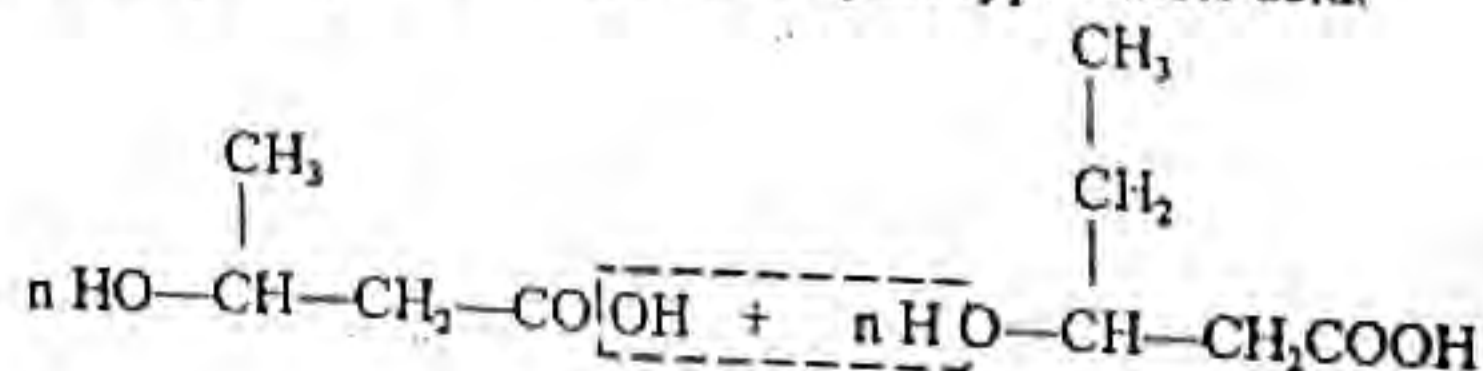
9.11 Bio Degradable Polymers

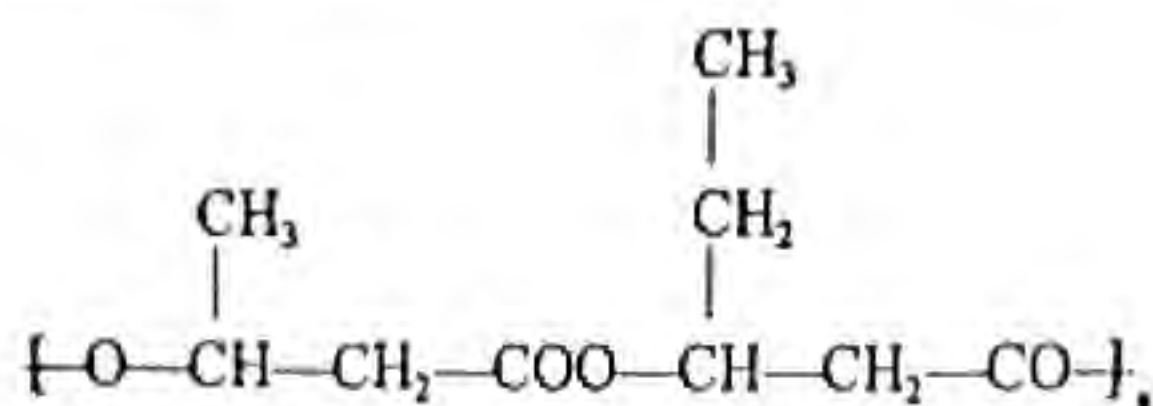
A huge amount of polymeric material is used in the world as plastics, fibers and elastomers. Fortunately these materials do not offer serious health problems though the main problem associated with the exceedingly large use of polymer is disposal of polymer waste. Two methods that can combat this problem, besides cutting down the use of polymeric materials to a certain extent, are their recycling or making them biodegradable. Use of biodegradable polymers not only offers an important means to fight against polymer waste disposal but also in biomedical polymers where one needs a non-toxic polymeric material that should in many cases be biodegradable.

A biodegradable polymer is one that would be decomposed by microorganisms. Though most commercial polymers in use today are nonbiodegradable, interest among the scientists and researchers is to produce cheap biodegradable polymers with desired properties to replace those nonbiodegradable polymeric materials in use.

Biodegradable polymers degrade mainly by enzymatic hydrolysis and in some cases by oxidation. Biodegradable synthetic polymers mostly have functional groups prevalent in proteins, polysaccharides and lipids.

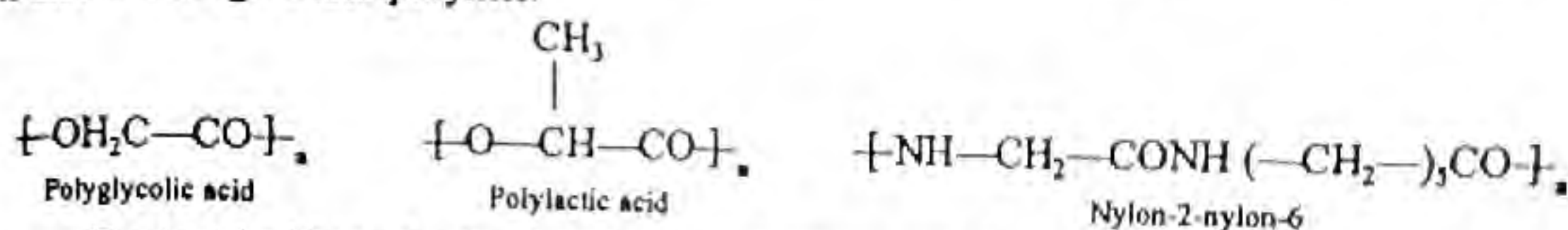
Poly(hydroxybutyrate-co- β -hydroxyvalerate), PHBV, is biodegradable polymer made by the condensation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.





It is used as packaging material, in orthopedic devices and in controlled drug release.

Polyglycolic acid and polylactic acid are the examples of biodegradable polymers used as sutures. Nylon-2-nylon-6, an alternating polyamide copolymer of glycine and 6-aminocaproic acid is also a biodegradable polymer.

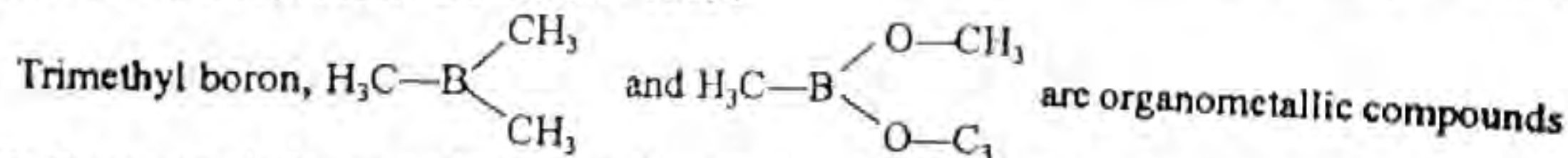


Dextron had been the first bioabsorbable suture made from biodegradable polyesters for post-operative stitches.

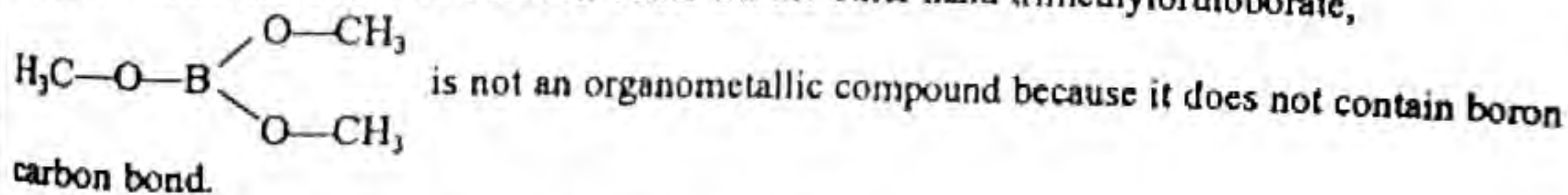
9.12 Organometallic Compounds

Definition : Organometallic compounds, are such compounds in which a metal atom is bonded directly to a carbon atom of a hydrocarbon molecule or radical. For example, diethyl magnesium ($\text{H}_3\text{C}-\text{H}_2\text{C}-\text{Mg}-\text{CH}_2-\text{CH}_3$) is an organometallic compound. It may be kept in mind that although such compounds as carbides, cyanide complexes and carbonyls do contain metal-carbon bonds yet these are not generally considered as organometallic compounds. However, many organometallic compounds of transition metals can be prepared from carbonyls.

The term metals is also conventionally extended to include elements less electronegative than carbon such as boron, silicon and arsenic. Thus :



because these contain boron carbon bond. On the other hand trimethylorthoborate,



Types of Organometallic Compounds

Organometallic compounds can be divided into simple and mixed compounds.

- I. **Simple organometallic compounds :** These are such organic compounds which have only hydrocarbon radical or hydrogen atom bonded to the metal atom. For example, lead tetraethyl $\text{Pb}(-\text{CH}_2\text{CH}_3)_4$ having hydrocarbon radical $(-\text{CH}_2\text{CH}_3)$ attached to Pb and $(\text{CH}_3)_3\text{SnH}$ having hydrocarbon radical $(-\text{CH}_3)$ as well as H-atom attached to Sn-metal are simple organometallic compounds. These are further subdivided into :

- (i) **Symmetrical** like $(C_2H_5)_2Hg$ and $(C_2H_5)_4Pb$. Here, the metal atom is bonded to same kind of hydrocarbon radicals.
- (ii) **Unsymmetrical** like $C_2H_5HgC_4H_9$ (butyl ethyl mercury). Here, the metal atom is bonded to different hydrocarbon radicals.

II. Mixed organometallic compounds : These are such organic compounds which have groups other than hydrocarbon radicals and hydrogen atoms attached directly to the metal. Some examples of such compounds are $(C_4H_9)_2SnCl_2$, $C_6H_5SbO(OH)_2$, C_6H_5MgBr , CH_3MgI etc.

Naming of Organometallic Compounds

These compounds are named by writing the name of the metal after the organic group such as alkyl, aryl etc. Some examples are :

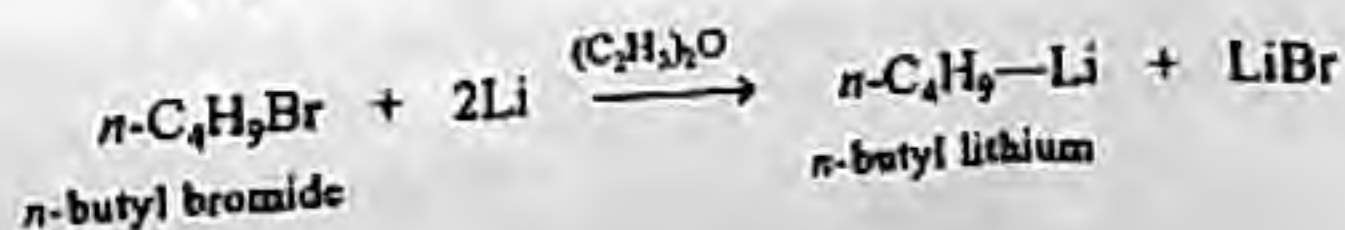
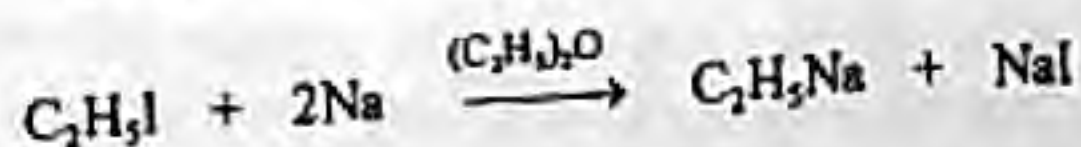
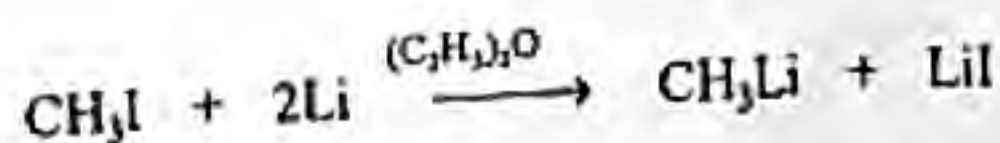
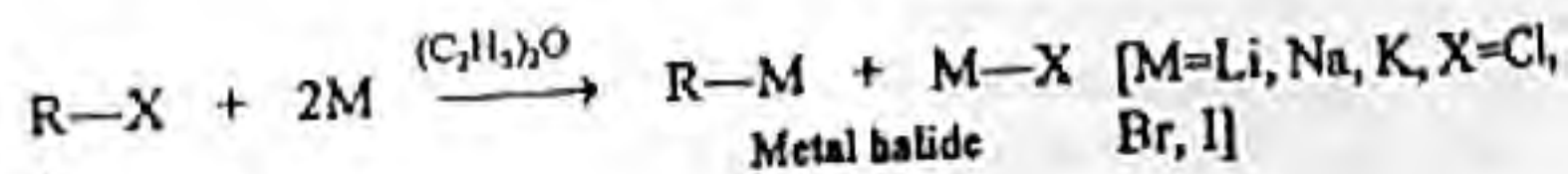
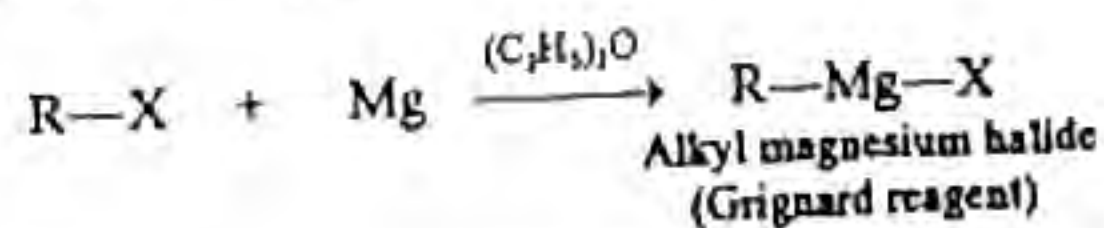
- (i) $(C_2H_5)_2Zn$ (Diethyl zinc)
 (ii) C_2H_5MgBr (Ethyl magnesium bromide)
 (iii) C_6H_5MgCl (Phenyl magnesium chloride)
 (iv) CH_3Li (Methyl lithium)

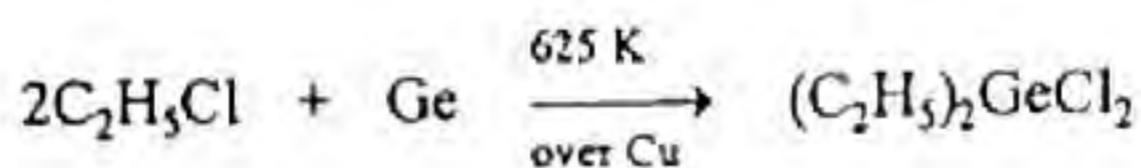
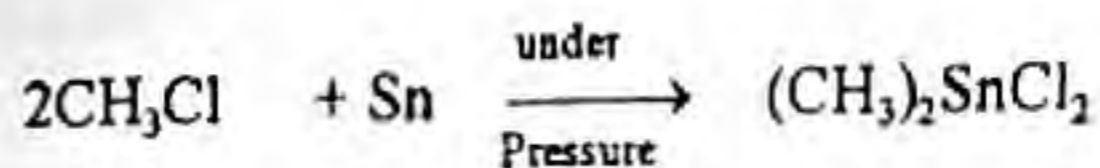
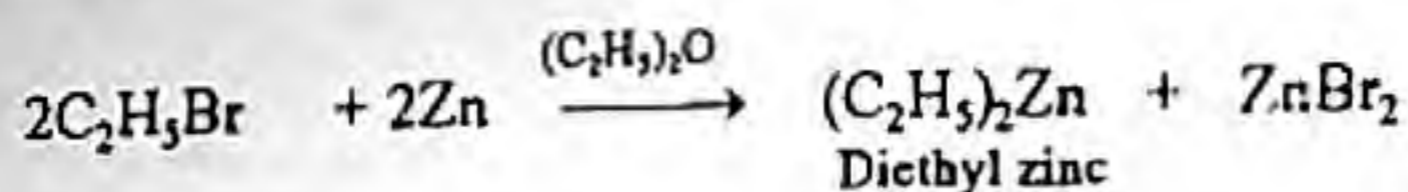
In order to name π -complexes, the number of carbon atoms which are bonded to the metal atom are indicated by the Greek letter, η (read eta or hepto). It is then followed by a number as $-\eta^2$, $-\eta^1$, $-\eta^4$, $-\eta^5$ etc., η^5 means that five carbon atoms are bound to the central atom. For example, $Fe(\eta^5-C_5H_5)_2$ is *bis* (cyclopentadienyl) iron.

Methods of Preparation (or Synthesis) of Organometallic Compounds

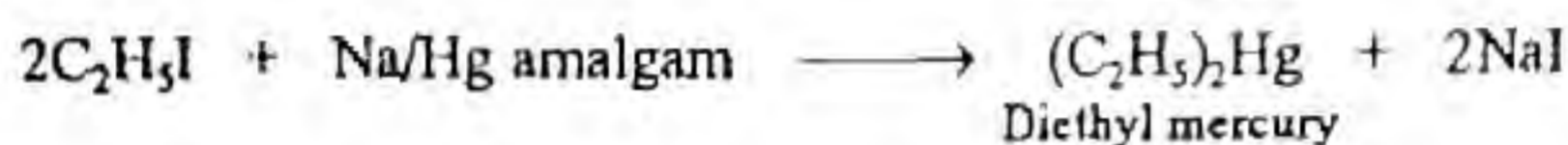
Following are a few methods to prepare organometallic compounds.

- By the direct action of metals :** When metals like Li, Na, K, Mg, Zn and Cd are treated with alkyl halides (RX) in presence of suitable organic solvent like diethyl ether, organometallic compound is formed. For example :

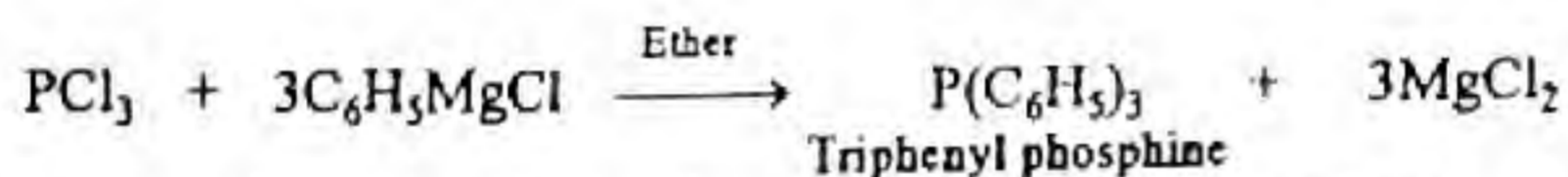
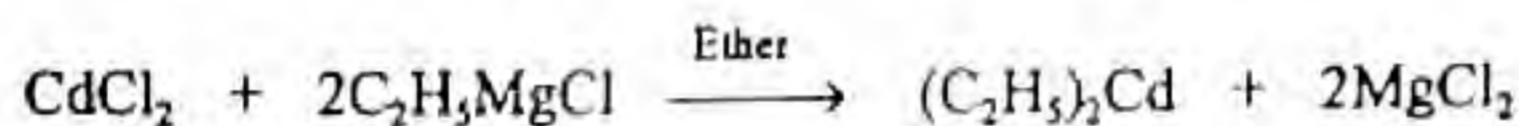
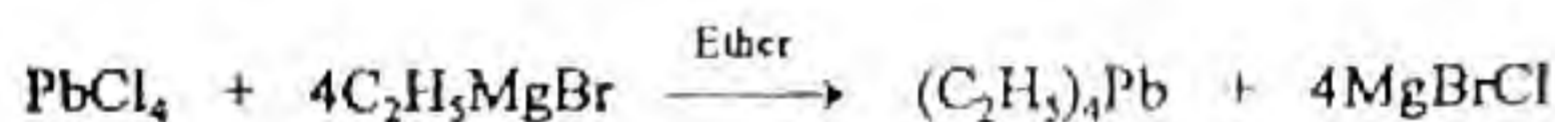
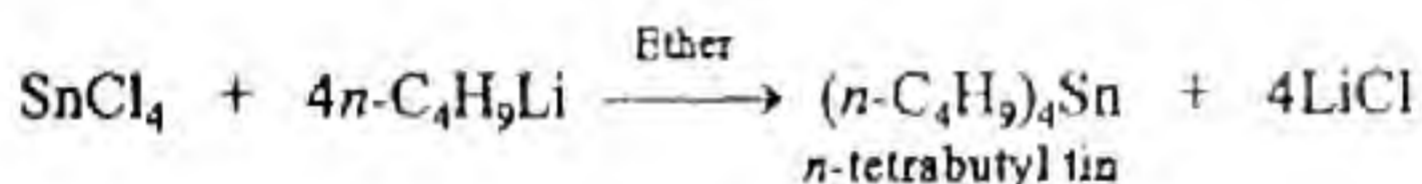




The metal is sometimes more reactive when present in an alloy or amalgam. For example :



2. **By the use of alkylating reagents :** When reagent like Grignard reagent and alkyl lithium reagents are made to react with halides of metals or non-metals in presence of ether as solvent, organometallic compounds are formed. For example :



3. **By metal exchange reactions,** organometallic compounds can be prepared.



4. These compounds can be prepared by alkyl halogen exchange reactions.

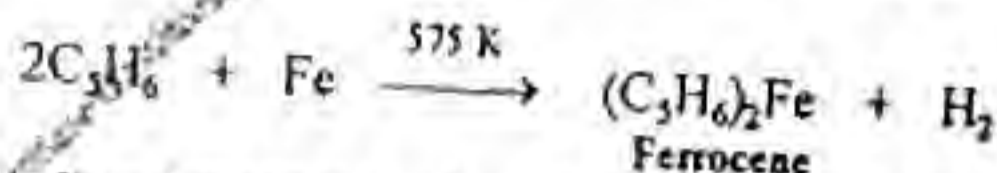


5. **Preparation of π -complexes :** A few methods to prepare π -complexes are given below :

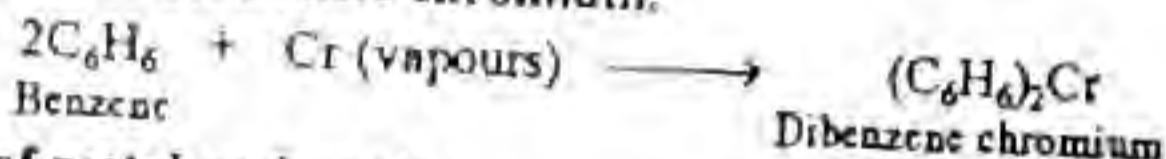
(a) **Preparation of Zeise's salt :** Zeise prepared the following compound from ethylene and potassium tetrachloroplatinate (II).

**(b) Preparation of ferrocene :**

(i) When cyclopentadiene (C_5H_6) reacts with iron at 575 K, ferrocene is obtained.



(ii) When cyclopentadienyl magnesium bromide is treated with Fe (II) chloride, ferrocene is obtained.

**(c) Preparation of dibenzene chromium.****6. Preparation of metal carbonyls :**

(a) When finely divided nickel is treated with carbon monoxide at 325 K, nickel carbonyl is formed.



This method is useful to purify nickel. The nickel carbonyl formed above on thermal decomposition gives pure nickel. It is called Mond's process.

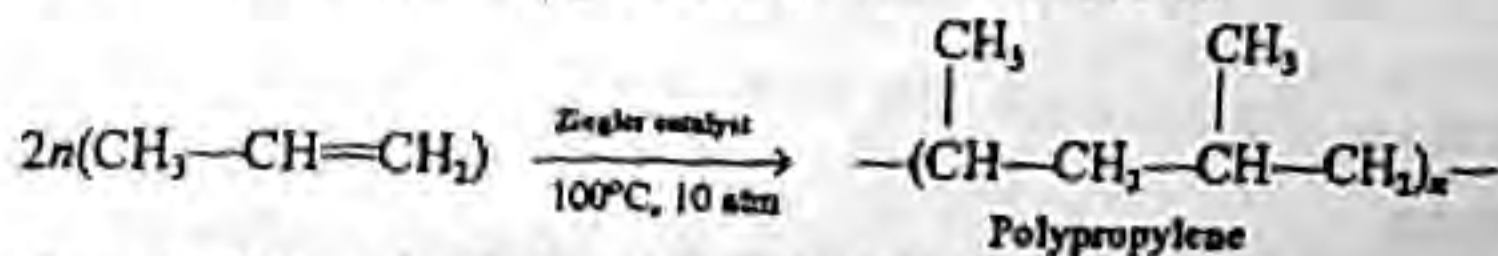
(b) When iron reacts with carbon monoxide at high temperature and pressure, iron pentacarbonyl is obtained.

**Applications of Organometallic Compounds**

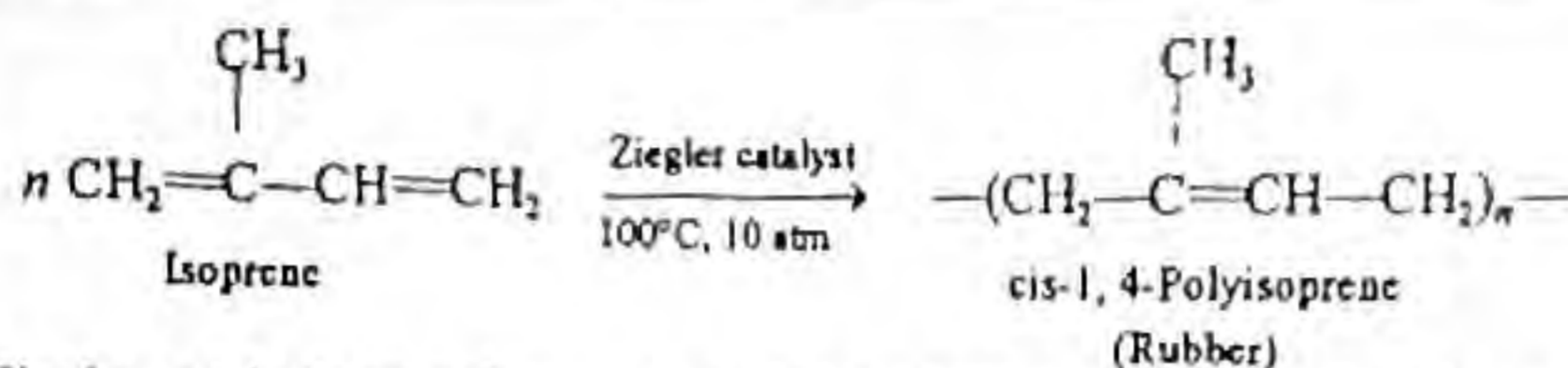
1. These are used in heterogenous catalysis, e.g., Ziegler Natta catalyst. Kurl Ziegler (of Germany) and Giulio Natta (of Italy) developed catalysts which permit stereoregular polymerization of alkenes of the type $\text{RCH}=\text{CH}_2$ (where $\text{R}=\text{H}$, alkyl or aryl).

Ziegler catalysts are a combination of organometallics which consists of a complex of triethylaluminium, $(\text{C}_2\text{H}_5)_3\text{Al}$ and a transition metal chloride, TiCl_4 . When these are mixed in a hydrocarbon solvent a heterogeneous precipitate develops which catalyses polymerization of alkenes at low temperature and pressure.

The method consists in passing the monomer, say propylene under 10 atmospheric pressure into an inert hydrocarbon solvent containing the catalysts at about 100°C .



Ethylene is polymerized to polyethylene in good yield at atmospheric pressure and room temperature by the use of Ziegler process. Isoprene was polymerized by Ziegler catalysts to a substance identical with natural rubber.



The impact of Ziegler catalysts on polymer chemistry has been so enormous that Ziegler and Natta were jointly awarded the Nobel prize in 1963. Before the development of Ziegler catalysts, nearly all addition polymerization involved free radical process with no regard to the stereochemistry of the polymer chain. Ziegler catalysts have revolutionized polymer chemistry since 1955. Developments since then has resulted in recognizing and gaining control to the stereospecific polymerization.

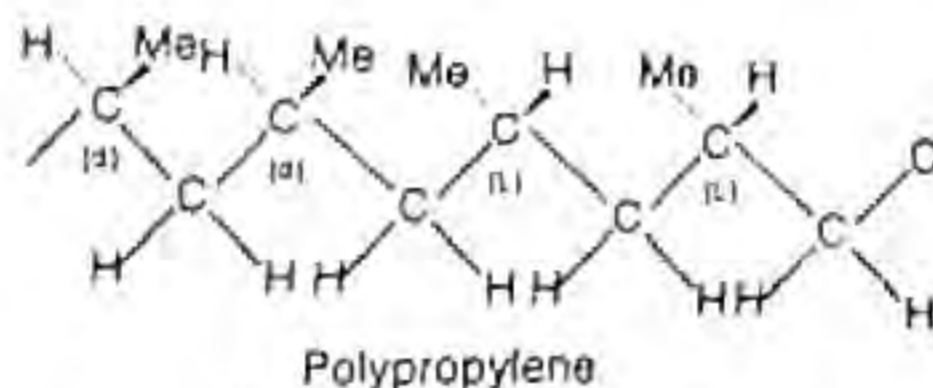
Polymer chains with branches or irregularly oriented bulky side groups are unable to lie alongside each other for steric reasons. Consequently, they have low crystallinity, are amorphous, low melting and mechanically weak.

Polymerization by radical process under high temperature and pressure gives highly branched polyethylene and irregularly oriented side groups (atactic) in polypropylene or polystyrene. In contrast, polymerization by the use of Ziegler catalysts under mild conditions produces unbranched polyethylene and stereoregular (isotactic) polystyrene or polypropylene.

Here in lies the usefulness of Ziegler catalysts which help the stereoregularity in the growing chain of the polymer. These stereoregular polymers are crystalline, high melting and mechanically strong.

Stereochemical Aspect

In polymers prepared from unsymmetrical ethylenes, e.g., propylene or styrene, every alternate carbon in the chain is asymmetric.



Me = -CH₃

For stereochemical purposes the carbon chain may be represented as -d-d-l-l-. The stereochemical sequence of the asymmetric carbons in a polymer chain is described by the term 'tacticity' which means the placement of the asymmetric carbon atoms in the chain.

If the stereo arrangement of the asymmetric carbons is

- (i) always the same, i.e., -d-d-d-d- or -l-l-l-l- it is called *isotactic*,
- (ii) alternating, i.e., -d-l-d-l-d-l- it is called *syndiotactic* and
- (iii) random, i.e., -d-l-d-d-l-l-l- it is called *atactic*.

Mechanism

Not much is known about the mechanism of polymerization by this catalyst. Several mechanisms have been suggested but none are so well substantiated. Polymerization by Ziegler catalysts is neither free radical nor ionic types. It is probably a coordination polymerization. As to