Unit-II

1. Phase: An introduction

A phase is defined as any homogeneous and physically distinct part of a system bounded by a surface and is mechanically separable from other parts of the system.

A phase may be gaseous , liquid or solid. It is perfectly homogeneous and distinct from every other phase that is present in the system. There must be a definite boundary between any two phases. This boundary is known as the interface.

Air constitutes a single phase only as it contains a mixture of nitrogen, oxygen, carbon dioxide, water vapour etc. A system consisting of only one phase is said to be ***homogeneous.***

A system consisting of more than one phase is said to be ***heterogeneous***. When various phases are in equilibrium with one another in a heterogeneous system, there can be no transfer of energy or mass from one phase to another. This means that at equilibrium, the various phases must have the same temperature and pressure and their respectively.

2. Phase Rule: Introduction

The phase rule was given by Gibbs, which explains the equilibrium existing in heterogeneous systems. Phase rule states that "*If the equilibrium between any number of phases is not influenced by gravity, or electrical, or magnetic forces, or by surface action but are influenced only by temperature, pressure and concentration , then the number of degrees of freedom (F) of the system is related to the number of components (C) and number of phases (P) by the following phase rule equation :*

$$F = C - P + 2$$

3. Explanation of terms

3.1 Phase (P)

A **phase** is defined as a homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces.

1. Liquid phase :

The number of liquid phase depends on the number of liquids present and their miscibility.

i) If two liquids are immiscible, they will form two separate liquid phases.

Example: benzene and water

ii) If two liquids are miscible they will form one liquid phase only.

Example: alcohol and water

2. Solid phase

Each solid forms a separate phase. The number of solid phase depends on the number of solids present in it.

Example: Many forms of sulphur can exist together, but these are all separate phases.

3. Gaseous phase

Since a gaseous mixture are thoroughly miscible in all proportions, it will form one phase only.

Example: a mixture of N_2 and H_2 forms one phase only.

4. A solution of a substance in a solvent consists of one phase only, e.g. glucose solution.
5. A heterogeneous mixture like:

$CaCO_3(s) \leftrightharpoons CaO(s) + CO_2(g)$

consists of three phases (i.e., two solids and one gaseous).

In the equilibrium reaction, Similarly, There are two solid phases, Fe and FeO and one gaseous phase consisting of $H_2O_{(g)}$ and $H_{2(g)}$. Thus three phases exist in equilibrium.

$Fe(s) + H_2O\ (g) \leftrightharpoons FeO(s) + H_2(g)$

6. At freezing point, water consists of three phases:

Ice (s) ⇋ Water (l) ⇋ Water vapour (g)

7. A homogeneous solid solution of a salt forms a single phase.

Example : Mohr's salt [$FeSO_4.\ (NH_4)_2SO_4.6H_2O$] solution has a single phase.

3.2 Component (C)

Component is defined as "the smallest number of independently variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation". While expressing the composition of a phase in terms of its components, zero and negative quantities are permissible. The components of a system do not represent the number of constituents or chemical individuals present in the system.

Example:

i)In the water system,

Ice (s) ⇋ Water (l) ⇋ Water vapour (g)

The chemical component of all the three phases is H_2O and therefore it is **one component system**.

ii) Sulphur exists in four phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition of all phases is S. Thus is an one component system.

$S_r \leftrightharpoons S_m \leftrightharpoons S_l \leftrightharpoons S_v$

iii) A system of saturated solution of NaCl consists of solid salt, salt solution and water vapour. The chemical composition of all the three phases can be expressed in terms of NaCl and H_2O. Therefore it is a **two component** system.

iv) In the thermal decomposition of $CaCO_3$,

$CaCO_3(s) \leftrightharpoons CaO(s) + CO_2(g)$

The composition of each of the three phases can be expressed in terms of at least any two of the independent variable constituents, $CaCO_3$, CaO and CO_2. Suppose $CaCO_3$ and CaO are chosen as the two components, then the composition of different phases is represented as follows:

Phase : $CaCO_3 = CaCO_3 + 0CaO$ Phase : $CaO = 0CaCO_3 + CaO$ Phase : $CO_2 = CaCO_3 - CaO$

Thus, it is a two component system..

v) Similarly,

$$Fe(s) + H_2O\ (g) \leftrightharpoons FeO(s) + H_2(g)$$

Here there are two solid phases, Fe and FeO and one gaseous phase consisting of $H2O(g)$ and $H2(g)$. Hence, there are *three* phases in equilibrium.

vi) In the dissociation of NH_4Cl, the following equilibrium occurs:

$$NH4Cl\ (s) \rightleftharpoons NH3\ (g) + HCl\ (g)$$

The system consists of two phass namely solid NH_4Cl and the gaseous mixture containing NH_3+HCl.

When NH_3 and HCl are present in equivalent quantities the composition of both the phases can be represented by the same chemical compound NH_4Cl and hence the system will be a one component system.

3.3 Degree of freedom

Degree of freedom is defined as the minimum number of independent variable factors such as temperature, pressure and concentration of the phases, which must be fixed in order to define the condition of a system completely.

A system having 1,2,3 or 0 degrees of freedom is called univariant, bivariant, trivariant and nonvariant respectively.

Example :

i) Consider the water system,

Ice (s) ⇋ Water (l) ⇋ Water vapour (g)

The three phases can be in equilibrium only at particular temperature and pressure. Therefore, when all the three phases are present in equilibrium, then no condition need to be specified. The system is therefore zero variant or invariant or has no degree of freedom. In this system if pressure or temperature is altered, three phases will not remain in equilibrium and one of the phases disappears.

ii) Consider a system consisting of water in contact with its vapour,

Water (l) ⇋ Water vapour (g)

To define this system completely, we must state either the temperature or pressure Thus degree of freedom is one and the system is univariant.

i) For a system consisting of water vapour phase only, we must state the values of both the temperature and pressure in order to define the system completely. Hence the system is bivariant or has two degrees of freedom.

ii) For a gaseous mixture of N_2 and H_2, we must state both the pressure and temperature, because if pressure and temperature are fixed, the volume automatically becomes definite. Hence, for a gaseous system, two factors must be stated in order to define it completely and thus, it has two degrees of freedom or bivariant system.

iii) Consider a system consisting of

$$NaCl_{(s)} \leftrightharpoons NaCl\text{-}water_{(aq)} \leftrightharpoons water\ vapor_{(g)}$$

we must state either the temperature or pressure, because the saturation solubility is fixed at a particular temperature or pressure. Hence the system is univariant.

Merits of the Phase rule:

1. It is applicable to both physical and chemical equilibria.
2. It requires no information regarding molecular/micro- structure, since it is applicable to macroscopic systems.
3. It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.
4. It helps us to predict the behaviour of a system, under different sets of variables.
5. It indicates that different systems with same degree of freedom behave similarly.
6. It helps in deciding whether under a given set of conditions:

a) various substances would exist together in equilibrium (or)

b) some of the substances present would be interconverted or

c) some of the substances present would be eliminated.

Limitations of Phase rule:

1. It can be applied only for system in equilibrium. Consequently, it is of little value in case of very slow equilibrium state attaining system.
2. It applies only to a single equilibrium system; and provide no information regarding any other possible equilibria in the system.
3. It requires at most care in deciding the number of phases existing in an equilibrium state, since it considers only the number of phases, rather than their amounts. Thus even if a trace of phase is present, it accounts towards the total number of phases.
4. It conditions that all phases of the system must be present simultaneously under the identical conditions of temperature and pressure.
5. It conditions that solid and liquid phases must not be in finely-divided state; otherwise deviations occurs.

4. Phase Diagram

Phase diagram is a graph obtained by plotting one degree of freedom against another. If the phase diagram is plotted between temperature against pressure, the diagram is called P-T diagram. P-T diagram is used for one component system.

If the phase diagram is drawn between temperature against composition, the diagram is called T-C diagram. T-C diagram is used for two component system.

Uses of Phase diagram

1. From the phase diagram, it is possible to predict whether an eutectic alloy or a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.
2. The phase diagrams are useful in understanding the properties of materials in the heterogeneous equilibrium system.
3. The study of low melting eutectic alloys, used in soldering, can be carried out using phase diagrams.

5. One-component system

5.1 Watersystem

The water system is a one component system

$$\underset{\text{(Solid)}}{\text{Ice}} \rightleftharpoons \underset{\text{(liquid)}}{\text{Water}} \rightleftharpoons \underset{\text{(gas)}}{\text{Vapour}}$$

Since water exists in three possible phases such as solid, liquid and vapour, there are three forms of equilibria

Liquid – vapour, solid vapour and solid liquid

Liquid ⇋ Vapour
Solid ⇋ Vapour
Solid ⇋ Liquid

Each equilibrium involves two phases. The nature of these phases which exist in equilibrium at any time depends on the conditions of temperature and pressure. These conditions have been determined and summarized in the pressure-temperature diagram in which pressure is treated as independent variable and is plotted along y – axis whereas temperature is plotted along x- axis.

From the phase rule, when C = 1,

$$F = C - P + 2 = 1 - P + 2 = 3 - P$$

That is the degree of freedom depends on the number of phases in equilibrium. Three different cases are possible:

(i) P =1 ; F = 3 – 1 = 2 (bivariant system)

(ii) P = 2; F = 3 – 2 = 1 (univariant system)

(iii) P = 3; F = 3 – 3 = 0 (invariant system)

The maximum number of degrees of freedom is two, hence, the phase diagram can be conveniently represented by a two-dimensional diagram on paper using pressure and temperature as variables.

The water system is shown in Fig.

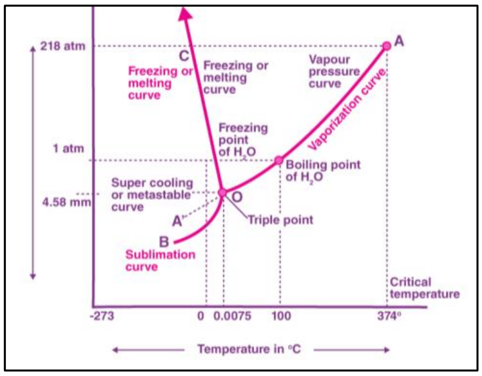


Fig: Phase diagram of Water System

The phase diagram for the water system is consists of

4.1.1 Areas

Area AOC, BOC, AOB represents water ice and vapour respectively. All these three areas consist of a single phase only. In order to define the system at any point in the areas, it is essential to specify both temperature and pressure. The degree of freedom of the system is two. i.e., Bivariant.

This is predicted by the phase rule

$F = C - P + 2$

$F = 1 - 1 + 2 = 2$ (bivariant)

4.1.2. Curves

There are three curves OA, OB and OC. Two phases exist in equilibrium along each of these curves. Hence, according to the phase rule equation

$F = C - P + 2 = 1 - 2 + 2 = 1$ (univariant or monovariant)

The system is univariant along each of these curves which means that to locate the position of any point along these curves, only one variable, either pressure or temperature needs to be specified. The various curves in the phase diagram are as follows:

1) Curve OA

The curve OA is called vapourisation curve**,** it represents the equilibrium between water and vapour. At any point on the curve the following equilibrium will exist.

$$\text{Water} \leftrightharpoons \text{water vapour}$$

The curve shows the vapour pressure of liquid water at different temperatures. The curve has its upper limit at temperature 374 °C and pressure 218 atm. This is the critical point beyond which the liquid phase merges into the vapour phase and they are no longer distinguishable from each other.

2) Curve OB

The curve OB is called sublimation curve of ice, it represents the equilibrium between ice and vapour. At any point on the curve the following equilibrium will exist.

$$\text{Ice} \leftrightharpoons \text{water vapour}$$

This equilibrium line will extend upto the absolute zero(-273^0C) where no vapour can be present and only ice will exist.

3) Curve OC

The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.

$$\text{Ice} \leftrightharpoons \text{water}$$

The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

4.1.3 Triple point (Point ‘O’)

At triple point all the three phases namely ice, water and vapour coexist. Thus the value of P is 3. Applying phase rule equation, F = C – P + 2 = 1 – 3 + 2 = 0 (invariant or non-variant)

the degree of freedom at this point is zero. It means that three phases can coexist in equilibrium only at a definite temperature and pressure. The values are 0.0075^0C and 4.58 mm respectively.

At this triple point, neither pressure nor temperature can be altered even slightly without causing the disappearance of one of the phases. The triple point is not the same as the ordinary melting point of ice (i.e, 0^0C). It's value has been increased due to the fact that 0^0C is the melting point of ice at 760mm of mercury and a decrease of 4.58 mm will rise the melting point to 0.0075^0C.

Metastable Curve OA' The dotted line OA' is the continuation of the vaporisation curve OA and represents the vapour pressure curve of supercooled water. This equilibrium is said to be metastable because it can be achieved only by carefully cooling water below O. This state *cannot* be achieved by the fusion of ice. Moreover, if an ice crystal is added to this system, then immediate solidification occurs and the temperature rises to 0 °C.

Region of the phase diagram	Phase in equibrium	No. of phases	F=C-P+2
	Areas		
BOC	Solid phase (solid ice)	1	2 (bivariant)
AOC	Liquid phase (liquid water)	1	2 (bivariant)
AOB	Vapour phase (water vapour)	1	2 (bivariant)
	Curves		
OA	Water ⇋ water vapour	2	1 (monovarient)
OB	Ice ⇋ water vapour	2	1 (monovarient)
OC	Ice ⇋ water	2	1 (monovarient)
OA'	Liquid ⇋ water vapour	2	1 (monovarient)
	Points		
O(0.0098 °C, 4.58 mm)	Ice ⇋ Water ⇋ vapour	3	0 (non-varient)

5.2 Sulphur System

It is a one-component, four-phase system. The four different phases of the sulphur system are

(i) Rhombic sulphur (S_R)

(ii) Monoclinic sulphur (S_M)

(iii) Liquid sulphur (S_L)

(iv) Vapour sulphur (S_V)

As the composition of all the four phases can be represented by one chemical compound, sulphur, it is a one-component system.

When C = 1, then from the phase rule equation

$F = C - P + 2$; $F = 1 - P + 2 = 3 - P$

The degree of freedom for different cases will be

When

P = 1; F = 3 – 1 = 2 (bivariant system)

P = 2; F = 3 – 2 = 1 (univariant system)

P = 3; F = 3 – 3 = 0 (invariant system)

P = 4; F = 3 – 4 = –1 (not possible)

$S_r \leftrightharpoons S_m \leftrightharpoons S_l \leftrightharpoons S_v$ (Never Exist)

Only three phases can be present at a time. In the sulphur system, one solid allotropic form transforms into the other. Such a system in which two or more solid states exist in equilibrium is called a polymorphic system. The phase diagram of Sulfur System is:

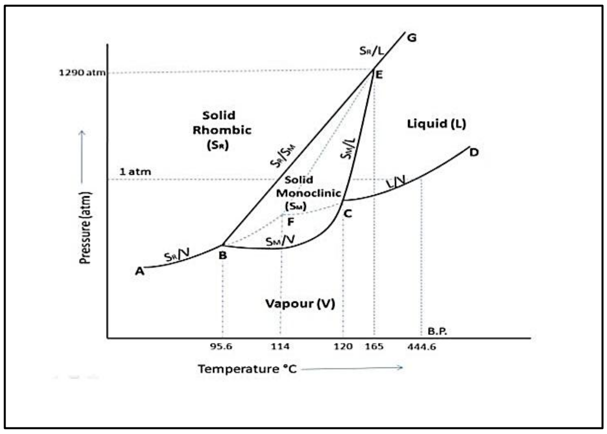


Fig: Phase diagram of Sulfur system

The phase diagram consists of the following:

1. Areas The phase diagram has four areas each of which consists of a single phase

Region of the phase diagram (Area)	Phases in equilibrium	Number of phases (P)	F=C-P+2
ABG	rhombic sulphur	1	1-1+2=2 (bivariant)
BECB	monoclinic sulphur	1	1-1+2=2 (bivariant)

GECD	liquid sulphur	1	1-1+2=2 (bivariant)
ABCD	vapour sulphur	1	1-1+2=2 (bivariant)

For each area, C =1; P =1, hence the degree of freedom will be

F = 3 – 1 = 2 (bivariant system)

Hence to locate the position of any point in these areas, both the variables—pressure and temperature—need to be specified.

2. **Curves** There are six curves in the phase diagram:

Region of the phase diagram(Curves)	**Phases in equilibrium**	**Number of phases (P)**	**F=C-P+2**
AB (vapour pressure of rhombic sulphur)	$S_R \leftrightharpoons S_V$	2	1-2+2=2 (univariant)
BC (vapour pressure of monoclinic sulphur)	$S_M \leftrightharpoons S_V$	2	1-2+2=2 (univariant)
CD (vapour pressure of liquid sulphur)	$S_L \leftrightharpoons S_V$	2	1-2+2=2 (univariant)
BE (transformation curve of S_M and S_R	$S_R \leftrightharpoons S_M$	2	1-2+2=2 (univariant)
CE (fusion curve of S_M)	$S_M \leftrightharpoons S_L$	2	1-2+2=2 (univariant)
EG (fusion curve of S_R)	$S_R \leftrightharpoons S_L$	2	1-2+2=2 (univariant)
Metastable curves		2	1-2+2=2 (univariant)
BF (metastable v.p curve of S_R	$S_R \leftrightharpoons S_V$	2	1-2+2=2 (univariant)
CF (metastable v.p curve of SL)	$S_L \leftrightharpoons S_V$	2	1-2+2=2 (univariant)
FE (metastable v.p curve supercooled rhombic sulphur)	$S_R \leftrightharpoons S_L$	2	1-2+2=2 (univariant)

3. Points

There are three stable triple points in the sulphur system: B (95.6 °C, 0.006 mm), C (120 °C, 0.04 mm) and E (151 °C, 1290 atm). Three phases exist in equilibrium along all these points.

B …… S_R, S_M, S_V

C .... S_M, S_L, S_V

E …… S_R, S_M, S_L

According to the phase rule equation, the degree of freedom along these triple points is

$$F = C - P + 2 = 1 - 3 + 2 = 0$$ (invariant or non-variant).

Metastable triple point F

The three metastable phases SR, SL and SV are in equilibrium at this point and the system is nonvariant.

Region of the phase diagram(Triple points)	**Phases in equilibrium**	**Number of phases (P)**	**F=C-P+2**
B	$S_R \leftrightharpoons S_M \leftrightharpoons S_V$	3	1-3+2=0 (invariant)
C	$S_M \leftrightharpoons S_L \leftrightharpoons S_V$	3	1-3+2=0 (invariant)
E	$S_R \leftrightharpoons S_M \leftrightharpoons S_L$	3	1-3+2=0 (invariant)
F(metastable)	$S_R \leftrightharpoons S_L \leftrightharpoons S_V$	3	1-3+2=0 (invariant)

6. Two-component system

Reduced phase rule or condensed phase rule.

We know the phase-rule equation,

$F = C - P + 2$

For a two component system, C = 2 and hence the above equation becomes,

$F = 2 - P + 2 = 4 - P$

When P = 1, the degree of freedom has the highest value.

$F = C - P + 2$

$F = 2 - 1 + 2 = 3$

The minimum number of phases in any system at equilibrium is one. It is clear from the equation, the maximum number of degree of freedom is three.

Thus, three variables – pressure, temperature and composition of one of the components must be specified to describe the system. This will lead to three dimensional figures which cannot be conveniently represented on a paper. To make this simple, one of the three variables is kept constant.

Hence,

we can have

(i) Pressure–temperature diagram (P–T) when composition is constant

(ii) Temperature–composition diagram (T–C) when pressure is constant

(iii) Pressure–composition diagram (P–C) when temperature is constant

In solid-liquid equilibrium of an alloy, practically there is no gaseous phase and the pressure will not have much influence. In the case of solid-liquid equilibrium, the experiments are generally carried out at constant pressure.

Thus the system in which only the solid and liquid phases are considered and the gas phase is ignored is called a **condensed system.** This reduces the degree of freedom of the system by one. The phase rule equation is then written as

$F' = C - P + 1$

This equation is called **reduced phase rule or condensed phase rule.** For a two component system the phase rule equation is written as $F' = C - P + 1$

$= 2 - P + 1 = 3 - P$

The above equation is known as the **reduced (condensed) form of phase rule for two component system.**

There are various types of solid-liquid equilibria of which only two of them are taken here.

1. Those equlibria in which the components are completely miscible with one another in liquid state. They do not form any compound on solidification. They give rise to merely an intimate mixture known as eutectic .

Some examples of this system are

1) lead-silver system
2) Lead-Antimony system
3) Zinc-cadmium system
4) Potassium iodide- water system

Those equilibria in which the components enter into chemical combination . They give rise to one or more compounds.

Examples of this system are :

5) Zinc-magnesium system
6) Calcium chloride – Potassium chloride system
7) Gold-Tellurium system.

Classification of two component system

The two component systems are classified into the following three types :

i) Simple eutectic formation
ii) a) Formation of compound with congruent melting point.
    b) Formation of compound with incongruent melting point.
iii) Formation of solid solution.

i) Simple eutectic formation :

A system with two substances which are completely miscible in the liquid state , but completely immiscible in the solid state is known as **eutectic system.** In this system the substances do not react chemically.

Among the mixtures of different proportions of two substances, the mixture which has the lowest melting point is known as the eutectic mixture.

The temperature and composition corresponding to the point eutectic point is called eutectic temperature and eutectic composition respectively.

ii) a) Formation of compound with congruent melting point :

In this type of binary alloy system the two substances form one or more compounds with definite proportions. Of the compounds, a compound is said to possess congruent melting point, if it melts exactly at a constant temperature into liquid, having the same composition as that of the solid.

b) Formation of compound with incongruent melting point :

Of the above compounds, a compound is said to possess incongruent melting point, if it decomposes completely at a temperature below it’s melting point yielding a new solid phase with a composition different from that of the original.

iii) Formation of solid solution :

In this type, when two substances, especially metals, are completely miscible in both the solid and liquid states, they form solid solutions where mixing takes place in the atomic levels. A solid solution can be formed only when the difference between the atomic radius of two metals is not greater than 15%.

Simple Eutectic System

The general phase diagram for binary alloy systems is shown in Fig. Here the pressure does not have the considerable effect. Hence, the other two variables viz, temperature and compositions are taken into account.

Components A and B.

When small quantities of B are added to A gradually, the melting point of A falls along the curve AC. In the same way when small quantities of A are added to B gradually, the melting point B falls along the curve BC. Hence, AC and BC are the freezing point curves of A and B respectively.

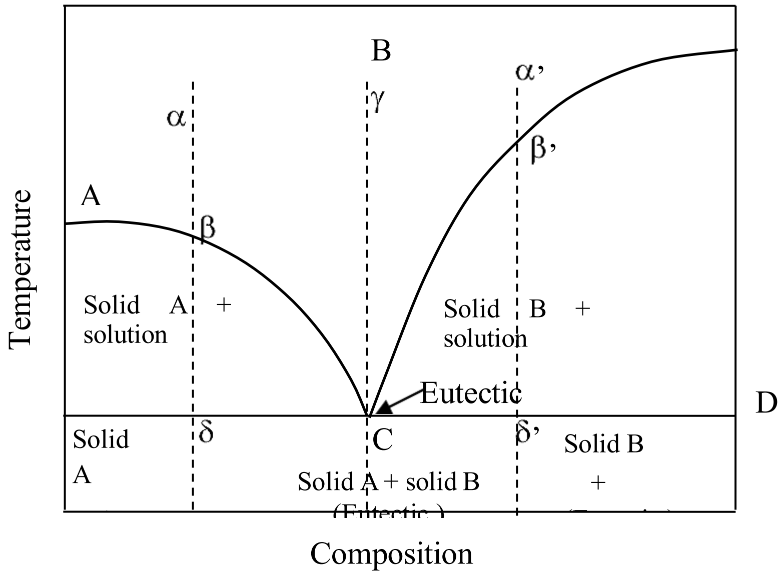


Fig: The simple Eutectic system

The curves AC and BC meet at the point C. At this point the three phases solid A, solid B and their solution coexist. The degree of freedom is zero here and the system is therefore invariant. Also only at this point C, the liquid can exist at the lowest temperature. Since the mixture of components A and B of composition corresponding to the point C has the lowest melting point, the point C is called the **eutectic point.**

Consider a liquid mixture of composition represented by a point cooled at constant pressure. The temperature falls without α any change of composition until the point on the curve AC is reached. At this temperature t_1, the solid A will separate out. The system β now consists of two pases and hence monovariant. As cooling continues, the component A keeps on separating out and the solution becomes relatively richer in B. The temperature and the solution composition both change along AC. Thus at the temperature t_1, solid A is in equilibrium with solution of composition X and at temperature t_2, it is in equilibrium with solution of composition Y. It is clear therefore, in the area ACD, solid A is in equilibrium with solutions of varying composition given by the curve AC depending upon the temperature.

When the temperature reaches a point represented by δ, the solid B also begins to separate out. On further cooling the system, solid A and B separate out together in constant ratio so that the composition of the solution remains constant. The temperature also remains constant for some time. When the liquid solution has been completely solidified and the system consists only of a mixture of solid A and B, it becomes monovariant. Further cooling will result in the fall of temperature below the line DD into the area in which only the two solids coexist as shown.

Characteristics of eutectic point

1. The system at eutectic point is invariant, the degree of freedom F = 0. For a two-component system, at eutectic point, C = 2, P = 3 (both the solids and their solution)

$F = C - P + 1$

$= 2 - 3 + 1 = 0$

2. It is the lowest freezing point of the system, that is, below this temperature, the liquid phase does not exist.
3. If the liquid is cooled below the eutectic point, both the components will solidify without change in composition.
4. Eutectics are mixtures and not compounds. When they were examined under an electron microscope, both the constituents are seen to lie as separate crystals. Moreover, physical properties such as density and heat of solution of eutectic solids were almost equal to the mean values of the constituents.
5. The alloys of eutectic composition have greater strength than their individual components because of their crystal characteristics.

Use of eutectic system Used for creating low melting alloys which can be made into safety fuses. Safety fuse is a device containing a small piece of low melting alloy that melts under excessive heat or excessive current.

Examples

1. Safety valve in pressure cookers is made of an alloy having a definite composition and definite eutectic temperature. As the temperature rises above this temperature, the alloy melts, preventing any accident.
2. Safety fuses are employed for plugs in water sprayers in buildings. In case of accidental fires, the plugs melt away and the water is released automatically to extinguish the fire.
3. Fuse wire used in electric circuits melts away on over-heating. *Solders* are readily fusible alloys which are applied to the point between metal objects to unite them closely without heating the objects to their melting point.

Examples of solders include

1. Soft solders containing 37–67% Pb, 31–60% Sn and 0.12–2% Sb, melts at low temperatures and are used for soldering electrical connections.
2. Brazing alloy containing 92% Sn, 5.5% Sb and 2.5% Ca is used for soldering steel joints.

In the same way, if the composition of liquid mixture is on the right of the eutectic point C, as represented by point 'similar series of changes will be obtained on cooling.

Construction of Phase diagram by Thermal analysis (or) cooling curve

Thermal analysis is a method involving a study of the cooling curves of various compositions of a system during solidification. The shape of the freezing point curves for any system, especially those involving metals can be determined by thermal analysis.

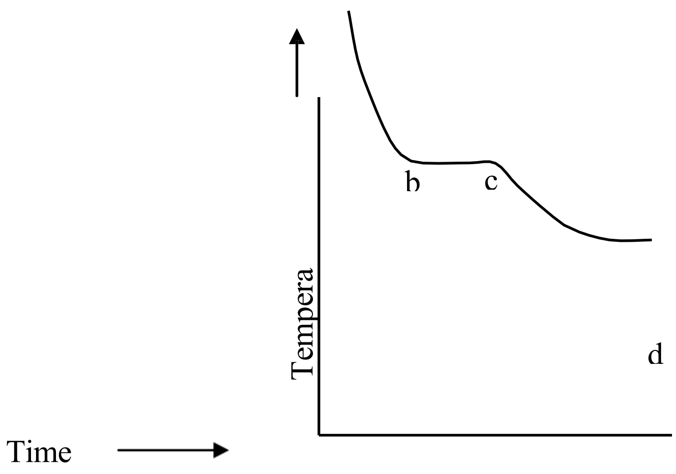
The data obtained from thermal analysis along with recorded curves are called as thermogram. These thermograms are characteristic of a particular system composed of either single or multi component materials. Thermograms indicate the system in terms of temperature, dependencies of it's thermodynamic properties. Let us discuss in detail the cooling curves or time-temperature curves of some simple systems.

Example 1 :

If a pure substance say x , in molten state is cooled slowly and the temperature is noted at different time interval. The graph plotted between temperature and time (the cooling curve) will be of the form shown in Fig(a). In this diagram ab denotes the rate of cooling of molten liquid and the liquid starts solidifying at the freezing point b. Now the temperature remains constant until the liquid melt is completely solidified. Solidification completes at the point 'c'. The horizontal line 'bc' represents the equilibrium between the solid and liquid melt. After the point 'c', the temperature of the solid begins to decrease along the curve 'cd'.

Example 2 :

When a molten liquid containing two components (say A and B) is cooled slowly then the cooling curve is different and one such curve is shown in Fig (b). As before, initially the rate of cooling is continuous. When it reaches the point 'b' one substance (either A or B) begins to solidify out of the melt, which is indicated by a break and the rate of cooling is different.



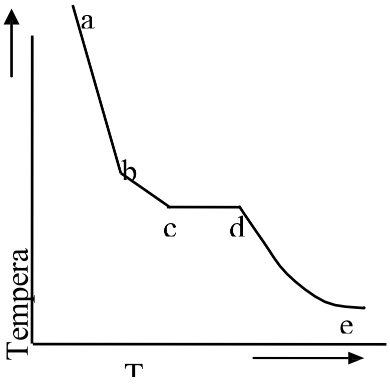


Fig (a) Cooling curve of a Pure solid

Fig (b) Cooling curve of a mixture A + B

On further cooling at the break point ‘c’ the second compound also begins to solidify. Now the temperature remains constant until the liquid melt is completely solidified, which forms the eutectic mixture (line cd) . After the break point ‘d’ cooling of solid mass begins. The temperature of horizontal line ‘cd’ gives the eutectic temperature.

The temperature measurements are done with a sensitive thermometer and the arrest points are determined with good precision.

A number of mixtures of A and B are taken with different composition. Each mixture is heated to the molten state and their cooling curves are drawn separately for each mixture. From the cooling curves of various compositions, the main phase diagram can be drawn by taking the composition in X-axis and temperature in Y-axis. Any point on this line indicates the appearance of the solid phase from the liquid. The area above this curve is only liquid phase.

Uses of Cooling curves

1. Cooling curves are used to find the percentage purity of the compounds.
2. It is used to find the melting point of the compounds
3. Thermal analysis is useful in derivation of phase diagram of any two- component system
4. Used to find the composition of the alloy.
5. Used to analyse the behaviour of the compounds.

6.1 Lead-Silver System

Lead–silver system is an example of a simple eutectic system. Silver and lead are miscible in all proportions and do not react chemically. When molten silver and lead are mixed together in all proportions, a single homogenous solution is formed. The system consists of four phases:

(i) Solid silver

(ii) Solid lead

(iii) Solution of molten silver and lead

(iv) Vapour

Since pressure has no effect on the equilibrium, the system can be represented by a temperature–concentration diagram at constant atmospheric pressure. As the gaseous phase is practically absent, one variable is neglected and the condensed phase rule

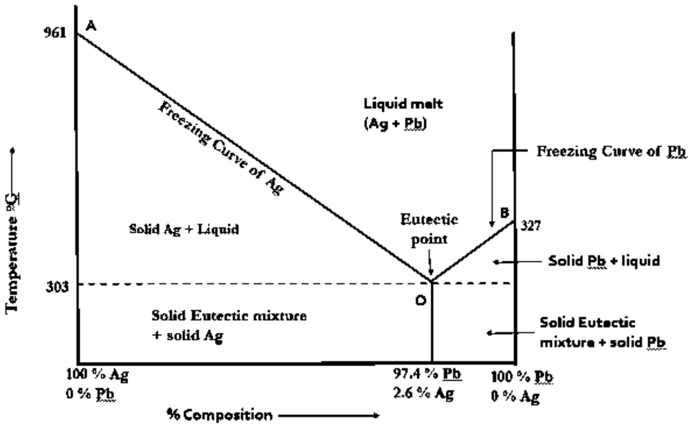


Fig: The Lead-Silver System

a) Points

Point A →Freezing point of pure Ag (961 °C)

Point B →Freezing point of pure Pb (327 °C)

Point O →Eutectic point (303 °C)

(b) Curves

Curve AO → Freezing point curve of Ag on gradual addition of Pb

Curve BO →Freezing point curve of Pb on gradual addition of Ag

(c) Areas

Area above AOB

Area ADOA

Area BOEB

Area below DOE

Points In the phase diagram, point A represents the melting point of pure Ag and point B represents the melting point of pure Pb. At these points, C = 1, P = 2 (pure Ag in equilibrium with its liquid or pure Pb in equilibrium with its liquid); hence, F = C – P + 1; 1 – 2 + 1 = 0.

Curves It is clear from the diagram that addition of Pb to pure Ag lowers the melting point of Ag; similarly, addition of Ag to pure Pb lowers the melting point of Pb. The curve AO represents the melting point of Ag on gradual addition of Pb. Along this curve, solid Ag and solution are in equilibrium.The curve BO represents the melting point of Pb on gradual addition of Ag. The curve indicates that the melting point of Pb gradually falls on addition of Ag. Along this curve, solid Pb and solution are in equilibrium.

Both AO and BO represent univariant systems

$$C = 2 \quad P = 2$$

$$F = C - P + 1 \; ; \; 2 - 2 + 1 = 1$$

Areas

Area above AOB It consists of only one phase (liquid solution). On applying the reduced phase rule equation, the degree of freedom comes out to be two. Hence, the system is bivariant and both temperature and composition are required to be specified to define the system completely

$$C = 2, \; P = 1 \quad F = C - P + 1$$

$$= 2 - 1 + 1 = 2$$

Area ADOA It contains two phases—solid Ag and solution containing Pb and Ag

Area BOEB It represents the phases—solid Pb + solution containing Pb and Ag. Both these areas have two phases and are univariant.

$$F = C - P + 1 \quad C = 2 \text{ (Pb and Ag)}$$

$$= 2 - 2 + 1 = 1 \quad P = 2 \text{ (Liquid + solid phase)}$$

Area below DOE It represents a solid mixture of Pb or Ag with eutectic. The number of phases is 2 (either Ag or Pb + eutectic) and the system is univariant.

$$C = 2, \; P = 2 \quad F = C - P + 1$$

$$= 2 - 2 + 1 = 1$$

Eutectic point O

The two curves AO and BO intersect at point O at a temperature of 303 °C. The point O is known as the eutectic point. At this point, three phases—solid Ag, solid Pb and the melt are in equilibrium. On applying the phase rule equation, we get

$$F = C - P + 1$$

$$= 2 - 3 + 1 = 0$$

Thus, the system at this point is invariant. Both temperature (303 °C) and composition (Ag 2.6% and Pb 97.4%) are fixed at this point. If the temperature is increased above the eutectic point, the solid phase (silver or lead) will disappear and if the temperature decreases below the eutectic point, the solution phase disappears and only the solid phase (eutectic + solid lead or silver) will remain.

Difference between melting point, triple point and eutectic point

- At melting point, a solid is in equilibrium with a liquid of the same composition.
- At triple point, three phases are in equilibrium.
- At eutectic point, two solids and a liquid are in equilibrium.

By definition, all eutectic points are melting points but the reverse is not true. Similarly, all eutectic points are triple point and not vice versa.

6.2 Zinc-Magnesium system

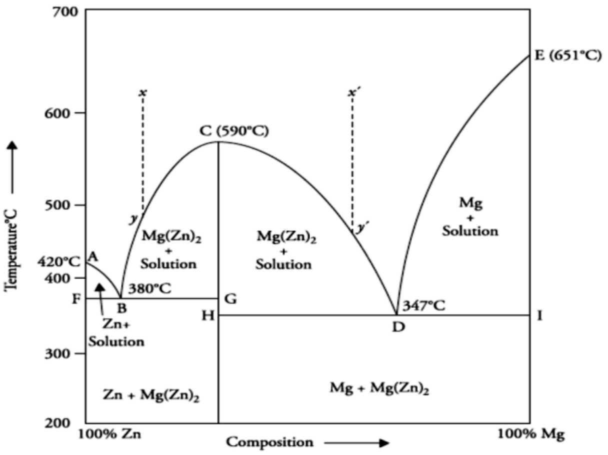


Fig: The phase diagram of Zinc-Magnesium system

a) Points

In the phase diagram, point A represents the melting point of pure zinc. Point E represents the melting point of pure magnesium and point C represents the melting point of Mg $(Zn)_2$. At each of these points, the value of C = 1, P = 2 (solid in equilibrium with the liquid of the same composition) Hence,

$F = C – P + 1; 1 – 2 + 1 = 0$

All these three points are invariant with zero degree of freedom.

Eutectic points There are two eutectic points B and D. At B, the three phases are zinc, Mg (Zn)2 and their melt. The eutectic temperature at B is 380 °C and the composition is 79% Zn and 21% Mg (Zn)2, whereas at D, the three phases are magnesium, Mg (Zn)2 and melt. The temperature at D is 347 °C and the composition is 61% Mg (Zn)2 and 39% Mg. Therefore, C = 2; P = 3 ; F = C – P + 1

2 – 3 + 1= 0 The system is invariant.

Region of the phase diagram	**Phases in equilibrium**	**Number of phases (P)**	**F=C-P+2**
A	Zn (s) ⇋ Zn (l)	2	1-2+1=0 (invariant)
E	Mg (s) ⇋ Mg (l)	2	1-2+1=0 (invariant)
C	$Mg(Zn)_2$ (s) ⇋ $Mg(Zn)_2$ (l)	3	1-2+1=0 (invariant)
B (eutectic point)	Zn, $Mg(Zn)_2$ and solution	3	2-3+1=0 (invariant)
D (eutectic point)	Mg, $Mg(Zn)_2$ and solution	3	2-3+1=0 (invariant)

b) Curves

Curve AB It is the freezing point curve of Zn. On gradual addition of Mg to Zn, the melting point of zinc is lowered along the curve AB. Along this curve, solid zinc is in equilibrium with the solution containing Zn and Mg. Thus, the number of phases is two. Applying the condensed phase rule,

$F = C - P + 1 ; 2 - 2 + 1 = 1$

Thus the system is univariant.

Curve ED It is regarded as the freezing or melting point curve of magnesium on gradual addition of zinc. Addition of zinc lowers the melting point of magnesium along the curve ED. Along this curve, magnesium is in equilibrium with a solution of Zn and Mg and the system is univariant.

Curve CB It represents the lowering of melting point of Mg (Zn)2 on addition of zinc.

Curve CD It represents the lowering of melting point of Mg (Zn)2 on addition of magnesium.

The curves CB and CD are univariant.

Region of the phase diagram (Curves)	**Phases in equilibrium**	**Number of phases (P)**	**F=C-P+2**
AB (Freezing point curve of Zn)	Zn (s) ⇋ Zn + Mg solution	2	2-2+1=1 (univariant)
ED (Melting point curve of Mg)	Mg (s) ⇋ Zn + Mg solution	2	2-2+1=1 (univariant)
CB (lowering of melting point of $Mg(Zn)_2$)	Addition of Zn	2	2-2+1=1 (univariant)
CD (lowering of melting point	Addition of Mg	2	2-2+1=1 (univariant)

of Mg $(Zn)_2$)			

c) Area

Region of the phase diagram (Area)	Phases in equilibrium	Number of phases (P)	F=C-P+2
ABFA	Solid Zn + liquid containing Zn and Mg	2	2-2+1=1 (univariant)
CBGC	Solid Mg (Zn)2 + molten Zn and Mg	2	2-2+1=1 (univariant)
CHDC	Solid Mg(Zn)2 + molten Zn and Mg	2	2-2+1=1 (univariant)
EDIC	Solid Mg + liquid containing zinc and magnesium	2	2-2+1=1 (univariant)
Area below FBG	Solid mixture of Zn + Mg(Zn)2	2	2-2+1=1 (univariant)
Area below HDI	Solid mixture of Mg+ Mg(Zn)2	2	2-2+1=1 (univariant)
Area above ABCDE	Molten Zn and Mg	1	2-1+1=2 (bivariant)

Cooling Consider a melt of composition represented by a point *x*. Allow it to cool along the line *xy*. When it reaches *y*, the solid Mg (Zn)2 separates out from the melt and the composition varies along the curve *y*B. At this point, there are two phases, and hence the system becomes univariant.

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

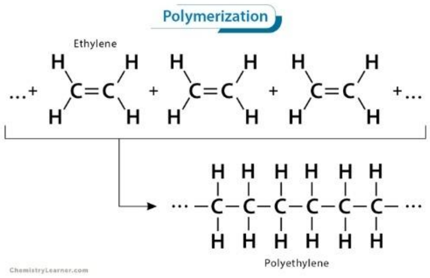
Similarly, if a melt of composition *x*' is cooled, the temperature will fall to *y*' without change in composition. At point *y*', Mg (Zn)2 separates and the composition varies along the curve *y*'D. At D, magnesium also separates out.

The phase diagram of the Zn–Mg system can be considered to be made up of two simple eutectic diagrams side by side, one on the left of CG and the other on its right. The curves BC and CD should meet to give a sharp point at C. The rounded maxima indicate that the compound formed is not very stable and dissociates partly. The dissociation of products in the liquid phase depresses the actual melting point of the compound resulting in a rounded melting point.

7.Polymer

7.1 Introduction

Polymers are compounds of very high molecular weights formed by the combination of a large number of small repeating units. The word 'polymer' is derived from the Greek word *poly* meaning 'many' and *mer* meaning 'part'. Polymerization reaction occurs when multiple monomers chemically bond together, forming large, complex structures. For example, many ethylene molecules combine to form a giant molecule of polythene.



The number of repeating units in a polymeric chain is called ‘degree of polymerisation’.

7.2 Classification of Polymers

Polymers may be classified in various manners.

Sr. no	Based on	Types	Examples
1	Origin	Natural polymer	Starch, cellulose
		Synthetic polymer	Polythene, PVC, Nylon
2	Monomer composition	Homopolymer	
		Copolymer (i) Random copolymer (ii) Alternating copolymer (iii) Block copolymer (iv) Graft copolymer	Copolymaer of butadiene and acrylonitrile SBS (shoe sole) High impact polystyrene
3	Chain structure	Linear	Polythene
		Branched	Low density polythene
		Cross-linked or network	Bakellite
4	Polymerisation mechanism	Addition polymer	Polythene, PVC
		Condensation polymer	Nylon
5	Molecular forces	Elastomers	Rubber
		Fibres	Nylon, silk, jute
		Thermoplastics	Polythene
		Thermosetting plastic	Bakellite
6	Tacticity	Isotactic	Polypropylene

		Syndiotactic	Syndiotactic polypropylene
		Atactic	PVC
7	Degree of polymerisation	Oligopolymers	
		Macromolecules	
8	Chain composition	Homochain polymer	Polythene, PVC
		Heterochain polymer	Nylon, terylene
9	Chemical	Organic polymer	Polythene, PVC
		Inorganic polymer	Silicon rubber, Phosphazene

7.3 Functionality

The number of bonding sites present in the monomers of the polymer is called functionality. For a molecule to act as a monomer it must have at least two reactive sites, that is, its functionality should be two. For example, ethylene can add two molecules of hydrogen or halogen. Hence, it is bifunctional (functionality two).

$$\mathbf{CH_2{=}CH_2 + H_2 \rightarrow CH_3 - CH_3}$$

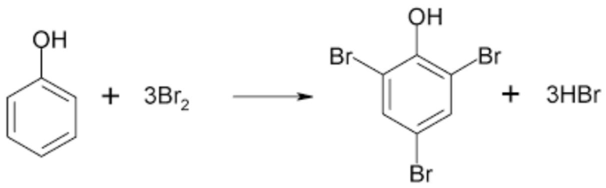
$$\mathbf{CH_2{=}CH_2 + Cl_2 \rightarrow CH_2Cl - CH_2Cl}$$

Similarly, acetylene has a functionality of four (tetrafunctional), as it can react with four atoms of hydrogen or halogen.

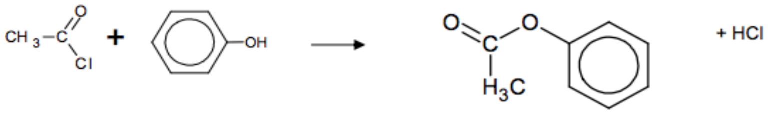
$$\mathbf{CH \equiv CH + 2H_2 \rightarrow CH_3 - CH_3}$$

$$\mathbf{CH \equiv CH + 2Cl_2 \rightarrow CHCl_2 - CHCl_2}$$

Similarly, phenol has three reaction sites (2-ortho and one para). It undergoes substitution reaction at these sites. Hence, it is trifunctional.



Phenol also exhibits a functionality of one as shown below.



Depending on functionality of the monomers used, we get linear, branched or three-dimensional cross-linked polymers. If the monomer is bifunctional (ethylene, propylene, vinyl chloride, styrene, etc.), a linear polymer is formed. A trifunctional monomer leads to the formation of a cross-linked polymer, whereas a mixture of bifunctional and trifunctional monomer may form branched or cross-linked polymer.

Bifunctional monomer- 2 reactive sites- linear polymer Eg: PE. PP, PVC (unsaturation)

Trifunctional monomer- 3 reactive sites- branched polymer Eg: Phenol, glycerol

Higher fuctinality monomer- 4,5 or more reactive sites- cross linked polymer Eg: Acetylene, urea, butadiene

7. Plastics

The term ‘plastic’ refers to the class of polymers that can be shaped into hard and tough utility articles by the application of heat and pressure. They are strong, light, highly dielectric, durable and corrosion-resistant. Because of these properties, the use of plastics is increasing tremendously. Plastic materials are replacing metals in all walks of life. The reason for using plastics over metals is that

- They are light in weight and at the same time possess good strength, toughness and rigidity.
- They are corrosion-resistant and also resist the action of chemicals.
- They are less brittle than glass and can be made equally smooth and transparent.
- They do not absorb moisture.
- They can be easily moulded into desired shape.
- They can take a variety of colors, are heat-resistant and abrasion-resistant, and have good dimensional stability. Their maintenance cost is low.

8.1 Types of plastics

Plastics are generally classifed into two categories:

(i) Thermoplastics

(ii) Thermosetting plastics

Thermoplastics They are plastic materials that soften on heating and can be moulded into desired shape. On cooling, they become hard. However, they can be resoftened and remoulded by the application of heat and pressure. The reason for resoftening of thermoplastic is that they are composed of linear or long-chain molecules. On heating the intermolecular bonds weaken, the material softens and thus can be moulded again without any damage. Common examples of thermoplastics are polyethene, polypropylene, polystyrene, teflon, polyamides, etc.

Thermosetting plastics They are those plastic materials that, when subjected to heat and pressure, change into a hard and rigid substance. Once they set, they cannot be softened again by the application of heat. The reason is that during moulding they acquire three-dimensional cross-linked structure. Such three-dimensional polymers will not soften when heated but may decompose or disintegrate at high temperatures. Common examples are bakelite, melamine formaldehyde, epoxy resins, etc.

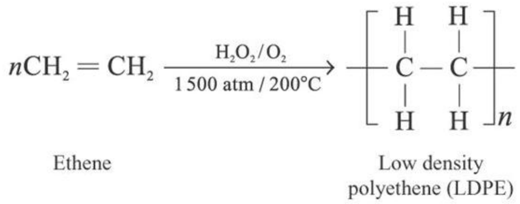
8. Individual polymers

8.1 Polyethylene plastics (Addition polymer)

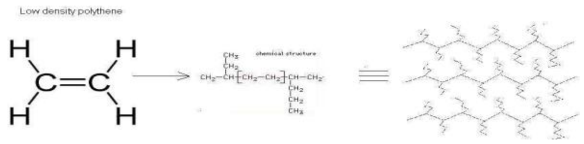
Polyethylene Also known as polyethene, it is an important thermoplastic resin prepared by the addition polymerisation of ethylene. It is of several types

(a) Low-density polyethene (LDPE)

Preparation It is prepared by the polymerisation of ethylene at high pressure (1000–3000 atmospheres) at 250 °C in the presence of free radical initiators like benzoyl peroxide. Traces of oxygen catalyse the reaction. In this process huge branched chains are formed through out every long back bone chain. The presence of branches repel each other and the long chains are not well fitted to each other having some gap produce low density (0.91 to 0.925 gm/cc) polymer.



$$nCH_2=CH_2 \xrightarrow[1500\ \text{atm}\ /\ 200°C]{H_2O_2/O_2} \left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}- \right]_n$$



Properties

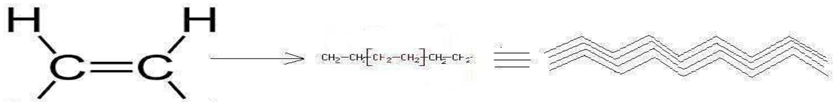
- It is a waxy solid that floats on water and has a linear branched structure.
- The branches do not allow the chains to pack efficiently; hence, its density is low (0.91–0.925 g/cm3). It is not polar and has weak intermolecular forces.
- It is tough, flexible, chemically inert and has excellent electrical insulation properties.
- Melting point $105 - 110^0$C.

Applications

a) As LDPE is a good insulator they normally used for the preparation of electrical wires and cables.
b) Pouch pack, squeeze bottles, delivery pipes are prepared from LDPE.
c) Toys, refill for ball pen and ball pen also prepared from LDPE.

(b) High-density polyethylene(HDPE)

Preparation



HDPE :No branch - well fitted to each other

The common method for the preparation of HDPE is by the polymerization of ethylene monomer at high pressure (30 - 35 atm) and temperature (70 − 200^{0}C) in presence of metal oxide catalyst like CrO_3 on silica alumina. High density polythene can be prepared by the polymerization of ethylene monomer at low pressure (5 - 7 atm) and temperature (60 − 70^{0}C) in presence of Zieglar Natta catalyst like triethyl aluminum and titanium tetrachloride. In this process of polymerization as there is absence of branch through out the long chain back bone, the chains are well fitted to each other which makes the polymer a high density (0.95 to 0.97 gm/cc) polymer.

Characteristics of high density polythene:

a) High density polyethylene have high density (0.95 to 0.97 gm/cc).

b) It is less branched.

c) Highly crystalline polymer having crystallinity 80-90 percent.

d) Chemically inert, nonpolar and having dielectric property zero.

e) Highly tough but flexible.

f) Melting point 130 − 135^{0}C.

Uses of high density polythene:

a) As HDPE is a good insulator they normally used for the preparation of high performance electrical cables.

b) Bucket, cup, toys are prepared from LDPE.

c) Due to inertness it is used for the storage of H_2SO_4, pipes for LPG gas and water reserver also.

(c) LLDPE (linear low-density polyethylene)

LLDPE can be prepared by the polymerization of ethylene monomer at 250^{0}C temperature and low pressure with alpha olefin (butadiene hexene or octene) in presence of Philips or Zieglar Natta catalyst like triethyl aluminum and titanium tetrachloride. The polymerization between ethylene and butane or hexene occur in gaseous phase and octene in solution phase. In this process the short branched chains are formed through out every long back bone chain. Due to presence of very short branches, density of the polymer lies in between LDPE and LLDPE (0.92 gm/cc) polymer.

LLDPE

Properties of linear low density density polythene:

a) Linear low density polyethylene have density in between low and high density polythene (0.92 to 0.925 gm/cc).

b) It is linear chain addition polymer with short branch.

c) Moderate crystalline polymer having crystallinity 70-75 percent.

d) Chemically inert, nonpolar and having dielectric property zero.

e) Moderately tough but flexibility more than LDPE.

f) Melting point $120 - 125^{0}$C.

Uses of low density polythene:

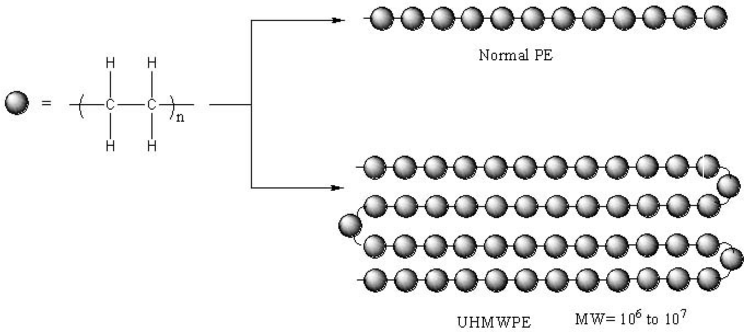
a) As HDPE is a good insulator they normally used for the preparation of covering electrical wires and cables.

b) Bag, polyethylene sheet, toys are prepared from LDPE.

c) Pouch bag pipes, bucket mug and flexible tube are prepared from LLDPE.

(d) Ultrahigh molecular weight polythene (UHMWPE)

Ultra high molecular Weight polyethylene is prepared from ethylene monomer by using of compres- sion moulding followed by ram extrusion gel spinning and by Kneading. Ultimately annealing of the polymer is done by heating the material at 135^{0}C temperature and cooling down at 5^{0}C temperature per hour up to 65^{0}C. Then the material is covered by heat insulating blanket for a day to bring down the temperature to room temperature.



Characteristics of ultra-high molecular weight polythene:

a) High density polyethylene has density is low (0.95 to 0.97 gm/cc).

b) Long back bone linear chain addition polymer having molecular weight 2 to 5 million or more.

c) Highly crystalline polymer having crystallinity 80-90 percent.

d) Chemically inert, nonpolar and having dielectric property zero.

e) It is also known as Plexi glass. It is colourless, transparent, amorphous and has good strength.

f) Highly tough, enormous tensile strength due to long back bone chain.

g) Highly resistance to abrasion and ultra violet radiation.

h) Melting point 135 – 145^0C.

Uses of ultra-high molecular weight polythene:

a) As ultra-high molecular weight poly ethylene have enormous tensile strength due to long back bone chain they are normally used for the heavy-duty gloves, armor for vehicle, preparation of high-performance electrical cables.

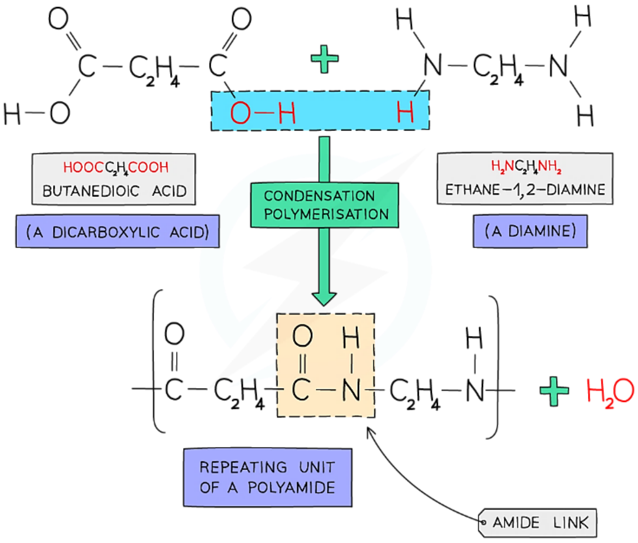
b) String for high performance bow.

c) As rope for climbing, suspension rope in parachutes.

8.2 Vinyl plastics (Condensation polymers)

(a) Nylon

- Nylon is a **polyamide** made from **dicarboxylic acid** monomers (a carboxylic with a -COOH group at either end) and **diamines** (an amine with an $-NH_2$ group at either end)
- Each -COOH group reacts with another $-NH_2$ group on another monomer
- An **amide linkage** is formed with the subsequent loss of one water molecule per link



- The structure of nylon can be represented by drawing out the polymer using boxes to represent the carbon chains.

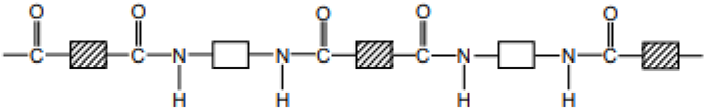


Fig: A section of Nylon-66

Nylon 6 It is produced by the self-condensation of aminocaproic acid.

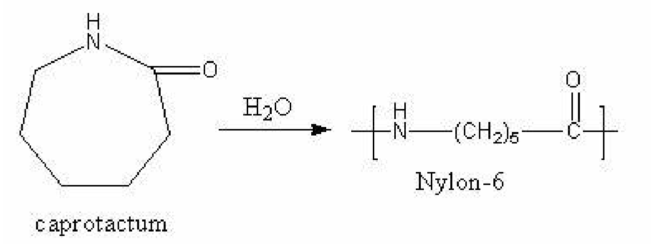


Fig: Synthesis of Nylon-6

Nylon-11

It is prepared by the self-condensation of 11-aminoundecanoic acid.

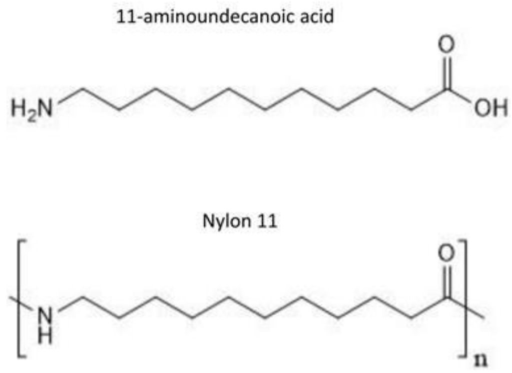


Fig: Synthesis of Nylon-11

Properties

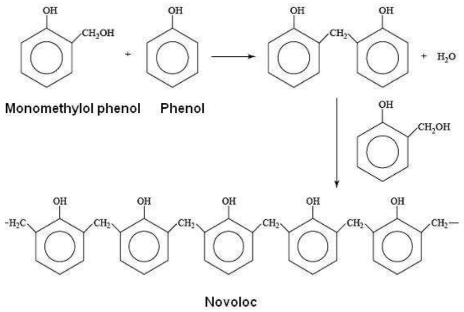
It is a linear polymer. The polymeric chains are held together by hydrogen bonding. They are translucent, high-melting polymers known for their toughness, abrasion resistance, elasticity and high crystallinity.

Applications Nylon 66 is used for making fibres that are used for making socks, undergarments, carpets, etc. It also finds use in mechanical engineering for the manufacture of gears, bearings, bushes, electrical mountings. Nylon moving parts work quietly without any lubrication. Nylon 6 is mainly used for making tyre cords. Bristles, brushes are generally made of Nylon 6, 10. Nylon-11 and Nylon 12 are used for making flexible tubings for conveying petrol. Glass-reinforced nylon plastics find use in domestic appliances, radiator parts of cars, etc.

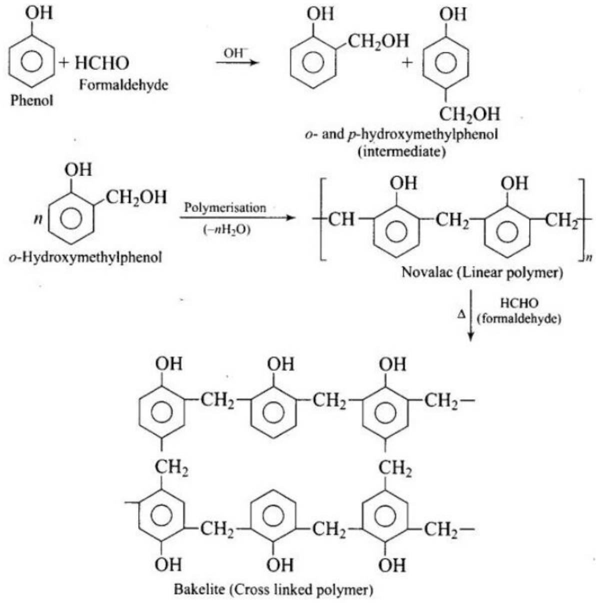
(b) Phenol-formaldehyde resin (Bakelite)

Commercially known as bakelite, this polymer is formed by the condensation of phenol and formaldehyde in the presence of acidic/alkaline catalyst. They are also known as phenoplasts and PF resins. Phenol–formaldehyde resins are normally prepared by two different methods.

(i) Base catalysed using excess of formaldehyde over phenol. The initially formed product called 'resole' changes into thermosetting polymer 'bakelite' simply by heating.



(ii) Acid catalysed method using excess of phenol.



Properties

Phenolic resins are hard, rigid, strong with excellent heat, moisture, chemical and abrasion-resistance. They are scratch-resistant and possess excellent electrical insulating properties.

Applications

They are used for making domestic switches, plugs, handles for pressure cookers, saucepans and frypans. They are also used for making moulded articles like telephone parts, cabinets for radio and television. They find use as adhesives for grinding wheels and brake linings. They are used in paints and varnishes, in the production of ion-exchange resins for water-softening and for making bearings used in propeller shafts for paper industry and rolling mills. Novoloc is used for the preparation of laminates. Resol is used for preparation of comb, P.O. Box, marine grade, shutter grade, Boilling water proff ply board, block board, flush door etc. Resol is used for preparation of electrical board, switch etc.

(C) Glyptal

Glyptal is formed by condensation polymerization of: - Phthalic anhydride (or maleic anhydride) - Glycerol or ethylene glycol Polymerization Reaction: Phthalic anhydride + Glycerol -> Glyptal (Polyester resin) + Water

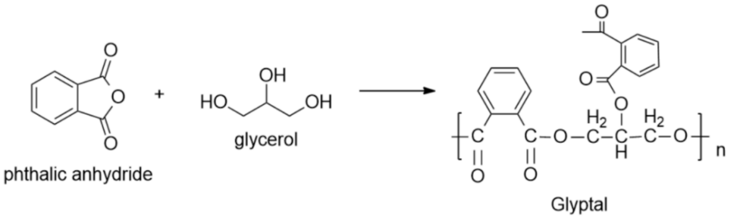


Fig: Glyptal synthesis

Properties: -

Glyptal is Hard and brittle than linear polymer. It does not soften when heated. The cross-linking keeps the polymer chains from moving with respect to one another when heated. It is a fast drying thermoplastic that can bond a variety of materials. It has strong, durable bonds that have excellent resistance to oil, gasoline and moisture.

Uses Glyptal and other alkyd polyesters are useful as coating materials and are not used for making fibres and plastic products. Glyptal was first commercialised in 1902 for use in paints and varnish industry. Glyptal is added in paints to improve their washability and adhesion. Its fast drying time alongwith its good dielectric strength makes it an excellent general-purpose adhesive for many electrical and non-electrical applications. It is also used as a sealing wax.

8.3 Speciality Polymers

8.3.1 Engineering thermoplastic -Polycarbonate

Polycarbonates are polyesters of phenols and carbonic acid. They can be prepared by the condensation of diphenoxymethylene derivatives with diphenyl carbonate. 2,2-bis(4-hydroxyphenyl) propane (bisphenol-A) on reaction with diphenyl carbonate gives polycarbonate.

Properties

Polycarbonate, a high-performance engineering thermoplastic, is a tough, strong, generally transparent, amorphous solid with outstanding impact resistance. It maintains its shape and size even under great stress over a wide range of temperature. It is resistant to water, acids, detergents, oils and greases, but is attacked by bases, halogenated solvents (chloroform, carbon tetrachloride), ketones (acetones, acetonitrile), organic solvents like benzene, benzylalcohol, dimethyl ether, carbondisulphide, etc. It has excellent resistance to high temperatures upto 140 °C and maintains toughness at low temperatures upto −20 °C. It has good electrical insulation properties.

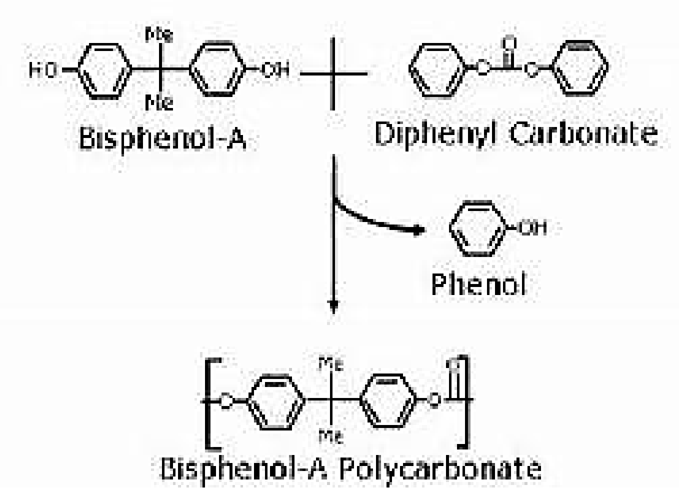


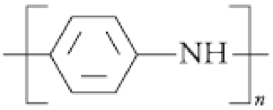
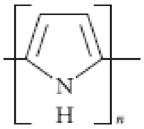
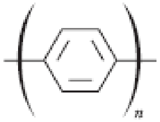
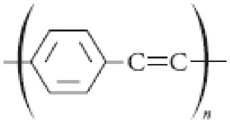
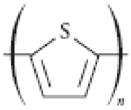
Fig: Synthesis of Polycarbonate

Uses

Owing to its electrical properties and dimensional stability, it is used for mouldings for computers, calculating machines, for making hair driers, electric razors, CDs and DVDs. Owing to its excellent impact resistance, it is used in automobile industry for making motorcycle windshields, police shields, headlight covers, car bumpers, front panels, safety helmets, etc. As it is not stained by oils, greases and domestic beverages, it is used for making blenders, food processing bowls, coffee maker, food mixer housings. Owing to its temperature resistance, stability and chemical inertness, it finds use in the manufacture of baby bottles, syringes. It is also used for making water dispensers, furniture (office and institutional), vacuum cleaner bases, cord hooks, impellers, spectacles, cameras and also for the manufacture of other unbreakable items.

8.3.2 Conducting polymer

The use of polymers is increasing rapidly in our day to day life. Because of their light weight, corrosion resistance, easily workability, easy maintenance they are replacing metals in all walks of life. The conductivity of doped ‘polyacetylene’ was found to be as high as 103 S cm–1. This is comparable to the conductivity of copper on an equal weight basis. The three scientists received the Nobel prize in chemistry in the year 2000 for their discovery and the development of electrically conducting polymers. After the above discovery, research continued in this field and a large number of electrically conducting polymers were discovered gradually. Some common conducting polymers are as Follows.

Conducting polymer	Repeating unit	Dopant	Conductivity (S cm^{-1})
Polyaniline		HCl	200
Trans polyacetylene		I_2, Br_2, Li, Na, AsF_5	10^4
Polypyrrole		BF_4^-, ClO_4^- , tosylate	500–7500
Poly(p-phenylene)		AsF_5, Li, K	10^3
Poly(p-phenylene vinylene)		AsF_5	10^4
Polythiophene		BF_4^-, ClO_4^- tosylate, $FeCl_4^-$	10^3

Classification of conducting polymers

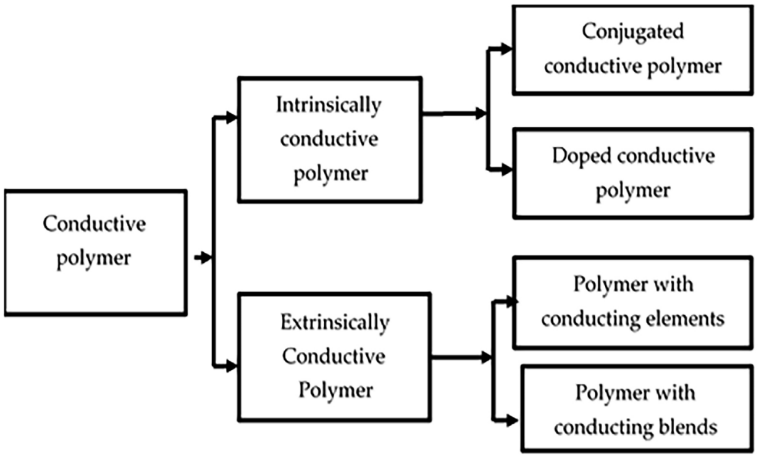
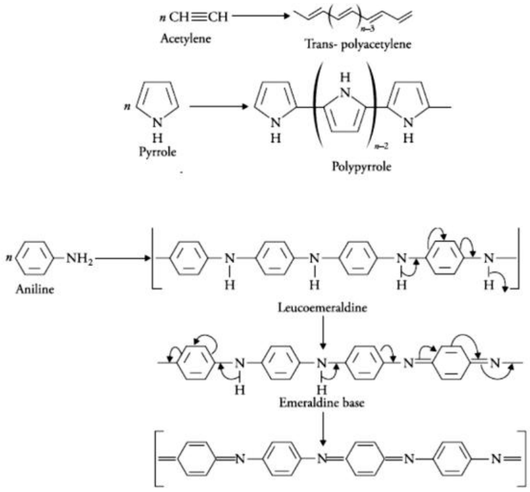


Fig: Classification of conducting polymer

Intrinsically conducting polymers -The conductance of these polymers is due to the extensive conjugation in their backbone. They are further of two types.

(a) **Conjugated *p*-electron conducting polymers** The conductivity of these polymers is due to the presence of conjugated *p* -electrons. The conjugated *p* electrons are delocalised. In an electric field, the *p* electrons get excited and are transported through the solid polymeric material. However, the conductivity of these polymers is not sufficient for their use in various industrial applications.

Example



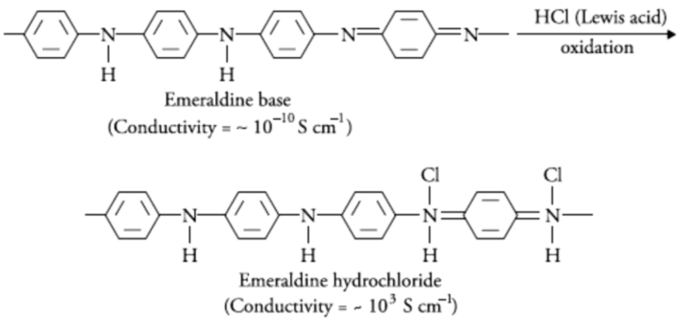
All the three forms of aniline conduct electricity. The conductivity of polyacetylene is 1.7 × 10–9 S cm–1 and that of polyaniline is 10–10 S cm–1. The conductivity is greatly enhanced by doping.

(b) **Doped conducting polymers** The polymers are doped by adding either electron donors or electron acceptors on the polymeric backbone. Doping can be of two types.

(i) **p-type doping** When the polymer is treated with a lewis acid, its oxidation takes place and holes (positive charges) are created on the polymer backbone. Commonly used p dopants are I2, FeCl3, Br2, AsF5, etc. For example,

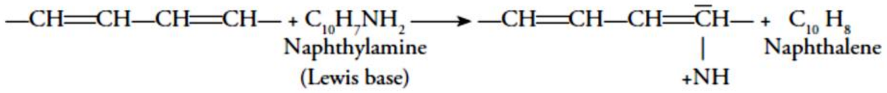
$$\underset{\text{Polyacetylene}}{(C_2H_2)_n} + \underset{\text{Lewis acid}}{2FeCl_3} \longrightarrow (C_2H_2)_n^+\ FeCl_4^- + FeCl_2$$

$$2(C_2H_2)_n + 3\,I_2 \longrightarrow 2\,[\,(C_2H_2)_n^+\ I_3^-\,]$$



Because of its conductivity it is also known as *synthetic metal*.

(ii) **n-type doping** When the polymer is treated with Lewis base, reduction takes place and negative charges are added on the polymeric chain. Some common n-type dopants are Li, Na, naphthylamine, etc. For example,



$$-CH{=}CH-CH{=}CH- + \underset{\substack{\text{Naphthylamine}\\ \text{(Lewis base)}}}{C_{10}H_7NH_2} \longrightarrow -CH{=}CH-CH{=}\underset{\substack{|\\ +NH}}{\overline{C}H}- + \underset{\text{Naphthalene}}{C_{10}H_8}$$

The conductivity of the above polymers depends on various factors.

(i) **Length of conjugation of the polymeric chain** Greater the conjugation level, more will be the delocalised electrons and greater will be the conductivity.

(ii) **Doping level** Conductivity increases with the increase in the amount of dopant.

(iii) **Temperature** Contrary to metals, the conductivity of these polymers increases with the rise in temperature.

Extrinsically conducting polymers

The conductivity of these polymers is due to presence of externally added ingredients. They are of two types.

Conductive element-filled polymers When the polymer is filled with conducting elements like carbon black, metallic fibres, metal oxides, their conductivity rises. Here the polymer acts as the binder of the conducting elements. However, addition of these elements affects tensile strength and impact strength of the polymer. This problem is overcome by blending a conventional polymer with a conducting polymer.

Blended conducting polymer Conducting polymers are added to conventional polymers. The blended polymers have better physical, chemical and mechanical properties.

Applications of conducting polymers

Conducting polymers find use in electronics, solar cells, displays, illumination sources and microchips. Some of the major application areas are

- In rechargeable light weight batteries. These have perchlorate-doped polyacetylene-lithium system. These batteries are light in weight, leak-proof and small in size.
- Used in photovoltaic devices like in Al/polymer/Au photovoltaic cells.
- In telecommunication systems.
- Electrically conducting polyaniline is used for antistatic coatings, and also for producing ‘smart windows’. Polyaniline shows different colors in different oxidation states. Hence, its color changes in response to sunlight or temperature changes.
- They are also used in organic light-emitting diodes (OLEDs).

- In electronic devices such as transistors and diodes.

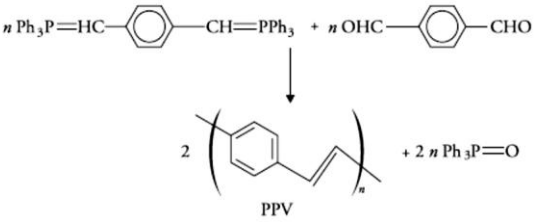
8.3.3 Electroluminescent Polymers

Electroluminescence is light emission stimulated by electric current. Electroluminescence in organic polymers has been known since early 1950s. Research continued and many organic polymers showing electroluminescence have been discovered. The phenomenon is particularly useful as enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDS, solar panels and optical amplifiers. A light-emitting diode (LED) is a crystalline semiconductor chip that glows. The first LEDs introduced in 1960s had only red and green colors. An OLED is made of sheets of polymer semiconductor material resembling plastic. Polymer LEDs were first discovered in 1989 by Richard Friend and co-workers at Cambridge University using polyphenylene vinylene (PPV) as the emissive layer.

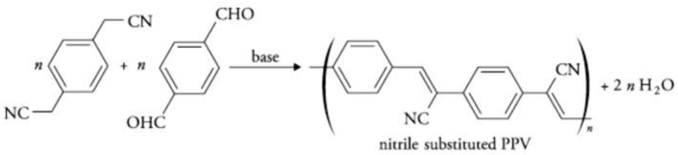
Polyphenylene vinylene It is the simplest and cheapest poly (arylenevinylene). It is the only polymer of this type that has so far been successfully processed into a highly ordered crystalline thin film.

Preparation

PPV can be synthesised by Witting-type coupling between bis (ylide) derived from an aromatic bisphosphonium salt and dialdehyde, especially 1, 4-benzenedialdehyde.



Knoevenagel condensation between a benzylic nitrile and an aromatic dialdehyde leads to the formation of PPV derivatives. Many side reactions occur in this method such as hydrolysis of nitrile group; hence, careful optimisation of the reaction conditions is needed.



Properties

- PPV is a bright yellow, fluorescent polymer. Its emission maxima is at 551 nm (2.25 eV) and 520 nm (2.4 eV). It lies in the yellow green region of the visible spectrum.
- It is insoluble, intractable and infusible. Incorporation of side groups like alkyl, alkoxy or phenyl increases the solubility of the polymer.

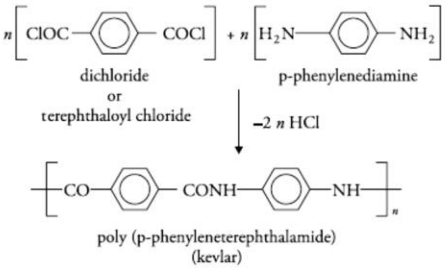
- It is a diamagnetic material with low intrinsic electrical conductivity (of the order of 10–13 S cm^{-1}). The electrical conductivity increases upon doping with iodine, ferric chloride, alkali metals or acids. However, the stability of these doped materials is low. Alkoxy substituted PPVs are easier to oxidise than the parent PPV and hence have much higher conductivities.

Applications

Owing to its stability, processability, electrical and optical properties, PPV has been considered for a variety of uses. As PPV is capable of electroluminescence, it is used in polymer-based OLEDs. Devices based on PPV emit yellow green light. Derivatives obtained by substitution of PPV are used when light of a different color is desired. PPV is also used as an electron-donating material in organic solar cells.

8.3.4 Liquid crystalline polymers

Liquid crystalline polymers are those polymers that are capable of forming regions of highly ordered structure while in liquid phase. The degree of order is somewhat less than that of a regular solid crystal. LCPs are very useful polymers because they have high mechanical strength at high temperatures. They also have extreme chemical resistance, inherent flame retardancy and good weatherability and are exceptionally inert. A very commonly known liquid crystalline polymer is kevlar. It is an aromatic polyamide, poly (p-phenyleneterephthalamide). It is prepared by the polycondensation of aromatic dichloride and aromatic diamines.



Properties

Kevlar has extraordinary mechanical properties, high elastic modulus and high tensile strength. Kevlar is known for its ability to be spun into fibres that have five times the tensile strength of steel and 10 times that of Al on a weight to weight basis. The high tensile strength is due to extensive hydrogen bonding between the adjacent polymeric chains. It has extreme chemical inertness, high heat stability and flexibility. It is also extremely resistant to fire.

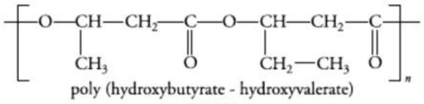
Uses

- It is used in the fabrication of protective wear including bullet-proof vests.
- It is extensively used in aerospace and aircraft industries, boat hulls, drum heads, sports equipments, car parts (such as tyres, brakes, clutch linings), helmets, brake pads, ropes, cables, etc.

- LCPs are generally used as reinforced (composite) materials with carbon or glass fibres.
- Presently, the high cost of liquid crystalline polymers limits its use to speciality applications like electronic components (e.g., computer memory modules), housings for light wave conductors and various aerospace applications.

8.3.5 Biodegradable polymers

Biodegradation is the degradation of a material by environmental factors such as sunlight, temperature changes or by the action of microbes (bacteria, fungi, etc.). The use of biodegradable polymers is increasing day by day. Many natural polymers like rubber and cellulose are biodegradable. They degrade gradually by bacterial action. Biodegradable synthetic polymers are polyvinyl alcohol, hydroxyethylcellulose polymer, polycaprolactone, polylactic acid, hydroxybutyrate polymer, hydroxyvalerate polymer and poly(hydroxybutyrate hydroxyvalerate) (PHBV) a copolymer of hydroxybutyrate and hydroxyvalerate. PHBV is a biodegradable aliphatic polyester.



$$\left[-\mathrm{O}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{O}-\underset{\mathrm{CH_2-CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}- \right]_n$$

poly (hydroxybutyrate - hydroxyvalerate)
PHBV

Applications

Biodegradable polymers find extensive use in the medical field. They are used commercially in tissue engineering and drug delivery field of biomedicine. Typical medical applications include the following.

- Use in orthopaedic fixation devices. Biodegradable polymers are used to join fractured bones. They provide the required strength to the bone and after the bone heals and can take the load, they harmlessly degrade over time. This prevents the patient from an additional operation for removal, as would be required if a metallic device was used.
- In controlled drug delivery, the polymer slowly degrades into smaller fragments releasing the drug gradually and in a controlled manner.
- It is used in dental devices, biodegradable vascular stents, biodegradable soft tissue anchors, etc. Biodegradable polymers are also being increasingly used in the manufacture of plastic bags, toys and other plastic products. These polymers gradually degrade in the environment (or in landfills) and leave the environment ‘greener’.