CHAPTER - 3

POLYMERS

INTRODUCTION :-

The polymer is defined as a large molecule built up by the repeatation of smaller units, which are joined by chemical bonds. The repeating unit is known as monomer from which the polymer is formed. There may be hundreds, thousands or even more molecules linked together. So, it can be said that polymer is a chain made up of monomers. The length of a polymer chain is decided by the number of repeating units in the chain. This number is called the degree of polymerisation. The molecular weight of the polymer is the product of molecular weight of monomer and the degree of polymerisation.

Most of the polymers have molecular weight between 10,000 to 10,00,000. So, polymer can be considered as a giant molecule. It is the giantness of the polymer that makes its behaviour different from that of monomer having very small size viz. monomers have sharp melting and boiling points, while polymers don't have sharp melting as well as boiling points. They soften first and turn into viscous molten mass. Further heating will turn polymers into a gas. But in the gaseous form, polymers no longer remain as polymers and are degraded into monomers. Solubility is also the property which gets affected by the gaintness of the molecule.

CLASSIFICATION OF POLYMERS :-

Polymer is the generic name given to vast number of materials of high molecular weight. These materials exist in countless forms and numbers;due to the various type of atoms present in the molecules. there has been a considerable confusion concerning the classification of the polymers. Polymers have different chemical structures, physical properties,mechnical behaviour, thermal characteristics etc. Depending on these properties polymers can be classified in the different ways as

1) NATURAL AND SYNTHETIC POLYMERS :-

Depending on their origin, polymers can be classified as natural and synthetic polymers. Polymers isolated from natural material called natural polymers. Typical examples are cotton, silk,wool,rubber,cellophone, cellulose,rayon RNA ,DNA etc.

Polymers synthesised from compounds having low molecular weight are synthetic polymers. Typical examples are polyethylene, PVC (polyvinylchloride) Nylon, Terylene, PUF (polyureaformaldehyde), polyamide etc.

2) ORGANIC AND INORGANIC POLYMERS :-

A polymer chain essentially made up of carbon atom in the backbone is termed as an organic polymer. The atoms attached to the backbone carbon atoms are usually hydrogen,oxygen, nitrogen etc. The majority of synthetic polymers are organic and they have been extensively studied. Infact, the number and variety of organic polymers is so large that when we refer to the term ' polymer ' we normally mean organic polymers. The polymer whose backbone chain generally contains no carbon atoms is termed as organic polymer. Silicon rubber, polysilicates are examples of inorganic polymers.

3) THERMOPLASTIC AND THERMOSETTING POLYMERS :-

The polymers which soften on heating, can be given any shape and which shall be retained on cooling, are called thermoplastics Examples are polyethylene,Nylon,polyvinylchloride,sealing wax etc. The polymers which undergo chemical change on heating, convert themselves into the fusible mass and which cannot be reshaped due to rigidity and hardness are called ' thermosetting polymers '. Examples of these are the phenolformaldehyde resins,epoxy resins,vulcanised rubber etc.

4) PLASTICS,ELASTOMERS,FIBERS AND RESINS :-

Depending on its form and use, polymers can also be classified as plastic, elastomer,fiber and resins. When polymer is shaped into the hard and tough utility articles by application of heat or pressure, They are called as plastics. Examples are polyethylene, polystyrene,PVC (polyvinylechloride) and PMMA (polymethylmethacrylate).

Polymers which can be converted into elastic materials having good strength and elongation,are termed as Elastomers e.g. natural and synthetic rubber,silicon etc.

Polymer which can be extruded into a thin filament like materials, are known as Fibers. Nylon and Terylene are the examples of them.

Certain polymers could be dissolved into the solvent and be used as adhesives for sealants. These polymers are called liquid resin. Examples are epoxy adhesives and polysulphide sealants.

5) ISOTACTIC,SYNDIOTACTIC AND ATACTIC POLYMERS :-

Depending of attachment of group to the backbone chain of polymer i.e. relative geometrical arrangement of groups, the polymer can be classified as Isotactic,sydiotactic and atactic polymers.

The polymers in which all side groups are attached on the same side of the backbone of the chain, are known as Isotactic polymers.

Those polymers in which side group are arranged regularly on alternate side of the chain are known as syndiotactic polymers.

while the polymers in which side groups are attached randomly on both side of the chain are known as atactic polymers

6) HOMOPOLYMERS AND CO-POLYMERS : -

A polymers in which entire chain is made up only of one monomer is called as Homopolymer. If the entire chain is made up of two or more monomers, then the polymer is known as co-polymer.

Further, co-polymers are classified as Random co-polymer, Alternating co-polymer, Block co-polymer and Graft co-polymer.

When two different monomers are randomly distributed throughout the chain, it is called a random co-polymer. When monomers are distributed alternately throughout the chain, it is called an alternate co-polymer.

When a sequence of definite monomer or block of one monomer is followed by block of another monomer regularly, then the polymer is called block co-polymer.

When a main chain is made up of only one monomer and branches are made up of other monomers attached to the main chain, the polymers are said to be graft co-polymer.

7) PHOTORESPONSIVE POLYMERS : -

Polymers that show property change in response to light are known photoresponsive polymers.

TECHNIQUES OF POLYMERISATION : -

Polymerisation can be carried out in all three phases viz, gas phase, liquid phase and the solid phase. The liquid phasepolymerisation is the most commonly used technique. The available techniques fall into two categories.

1) Polymerisation in homogenous system
2) Polymerisation in heterogenous system

When the monomer, the solvent (if used) and other ingredients are all in the same and miscible phase, then polymerisation is termed as homogenous polymerisation. But if some of them are immiscible with each other, it is termed as heterogeneous polymerisation. Different techniques employed for synthesis of a polymers are described below.

1) Bulk polymerisation
2) Solution polymerisation
3) Precipitation polymerisation
4) Suspension polymerisation
5) Emulsion polymerisation
6) Interfacial polymerisation
7) Solid phase polymerisation

1) Bulk polymerisation : -

This is the most simple form of polymerisation. The polymerisation of pure monomer without diluent is called bulk or mass polymerisation In this technique the monomer is purified to remove oxygen and other inhibitors. The polymerisation

is started through heating, UV light exposure or adding initiators. Once the polymerisation starts, the reaction mixture heats itself and reaction proceeds automatically with increase in conversion of monomers to polymers. As viscosity of the mixture increases, the conversion becomes more and more difficult, therefore, bulk polymerisation with large amount of monomers become explosive due to increase in temperature. The difficulty in heat removal is the main reason why few bulk polymerisations are carried in the industries. polymer with high molecular weight can be obtained. One of the characteristics of bulk polymerisation of technical
advantage is the great purity of polymer resulting from the lack of additives during polymerisation.

2) Solution polymerisation : -

If monomer is added to inert solvent, then polymerisation can be controlled easily. The solvent is chosen in such a way that it boils at the desired (required) temperature of polymerisation. In that case evaporated solvent can be reused after cooling. The concentration of the solvent is so chosen that the polymerisation mixture can still be stirred after complete conversion. Solution polymerisation has been employed almost in all cases were the polymer is used in the form of solution. To obtain a pure polymer by distilling off the solvent is relatively complicated. Chain transfer with solvent, yields low molecular weight polymer by solution polymerisation than that by bulk polymerisation. This type of polymerisation has two advantages viz. the reactor works always in a range of high polymerisation rates and molecular weight distribution curve is not as broad as with the polymers produced in a discontinuous process with high conversion.

3) Precipitation polymerisation : -

Not all polymers are soluble in the monomers from which they are prepared e.g. polyvinyl chloride is insoluble in vinyl chloride. These polymers precipitate during polymerisation first as Gel particles and then become white, more or less a fine powder. Precipitation occurs when one reaches a certain concentration of polymers.

4) Suspension polymerisation : -

If a water insoluble monomer is mixed intensively with three to four times of water gives a system wherein the monomer is suspended in a aqueous phase, in the form of small spheres of 0.1 - 1 mm diameter. By the addition of catalysts and by heating, polymerisation can be started in few hours, the monomer droplets become highly viscous and sticky. The whole mass coagulates into a gel like precipitate, which can continue to polymerise. Mass coagulation is observed because it becomes more difficult separate small droplets due to the increasing viscosity and stickiness of the solution. This coagulation can be prevented by addition of hydrophilic protective colloids, which can later be removed by intensive washing with water. polymers obtained by this technique are hard, glassy, pearls. The size of the pearl depends on the stirring rate. Slow stirring gives bigger pearls while fast stirring gives smaller pearls.

5) Emulsion polymerisation : -

In emulsion polymerisation, the liquid monomer is dispersed in a liquid with which it does not mix, to form an emulsion. The usual dispersion medium is water. Emulsifiers are surfactants i.e. surface active agents which absorbs at the water monomer interface. Essentially, the function of the emulsifier is to form mechanically stable absorption layers which prevent merging of monomer or polymer droplets. Hence the substances used as emulsifiers usually contain a polar group and a comparatively large hydrocarbon radical. Polymer emulsion in water resulting from the emulsion polymerisation are called synthetic latex. The latex is purified by the usual method of coagulating colloidal systems.

6) Interfacial polycondensation : -

Polyesters and polyamides are usually prepared by the reaction of glycol and diamine with carboxylic acid. If one use acid chloride, then polymerisation can be carried out in elegant manner in the two phase system. Thus, a layer of dilute aqueous solution of diamine on top of a dilute solution of acid chloride in a solvent such as carbontetrachloride, not miscible with water and the interface is formed. At the interface, a very thin film of polymide is formed instantaneously and this film can be removed with a glass rod wound up on the rod or roller. If the concentration of monomers have been selected properly, the thread of the polymer formed could be wrapped on rod or roller continuously. When solution becomes dilute, the thread breaks, with an exception of the polycarbonate synthesis.

7) Solid phase polymerisation : -

Many monomers are capable of polymerising not only in the liquid phase but also in the crystalline state, below their melting points. Such a polymerisation is initiated by irradiating the monomer, may affect the rate of change propagation, structure and packing of the polymer. On approaching the melting point, the rate of polymerisation of a solid monomer increases sharply and often turns out to be higher than the rate of polymerisation of the same monomer in liquid phase.

APPLICATIONS OF POLYMERS [1,2]:-

Polymers find their applications in all the facets of our life, because of the wide range of properties and possibilities of modifying them as per our requirements. Polymers have replaced metal and wood, glass, ceramic in the wide variety of industries including packing, consumer products, automobiles, buildings and construction, electronics, electrical equipment, heavy industrial equipment etc They are widely used for transportation, communication, public health, electrical and textile industry, storage purpose, medicine and surgery, agriculture, solar cell etc. Finding so many applications of polymers, it can be said that we are living in the **POLYMER AGE**.

Electrical conduction was found out for highly condensed polycyclic aromatic hydrocarbons which resembles the graphite for molecular structure. A number of polymers [3,4] have been studied extensively and found to fall into the family of semi-conductors. Metallic conductivity in polymer was first found out in poly (sulfur nitride) [5] in 1973. In 1975, same polymer was found to transform into superconductor [6] and model for the same was also proposed [7] In recent years, interest in utilizing the polymers in biomedical field is increasing rapidly. The pioneering work of Wichterele and Lim [8,9] for using polymer for soft contact lenses revolutionized the industry. Artificial skin, artificial liver, artificial kidney, lung membranes and heart were prepared artificially from the biopolymers. Recently artificial nose was prepared which can sense three types of smell. In the aerospace industry, resinous polymers encompass a wide variety of hardware applications for aircraft, missiles and space structure. In aircraft resins are uses matrix material for primary and secondary fiber reinforced composite structures. Resins also used as adhesives and sealants. Missiles applications include equipment sections, meter cases etc. Polymers are used to construct telescopes antennas and satellites. Different polymeric resins are used in Army for the construction of light weight rifles,machine guns etc. Important applications of polymers in the Navy are in the construction of life bats, pleasure crafts, boat hulls, propeller shafts, thermal insulations, gaskets, and acoustically transparent and absorbing materials.

Blends of polylfins are used in automobile industry for bumper coverings, wheel bearings and flaps, dashboard, steering wheel coverings, door pockets, radiators, grills etc. Other field of applications include the shoe industry, sanitary and installation engineering, sports equipments bags and suitcase

Polyvinylchloride is used for profile the manufacture of widow, guttering and street direction signs, gas pipes, cladding panels, equipment for chemical industries, refrigerators, flame resistant watt coverings, casing for electrical tools, safety helmets, computer parts etc. Polystyrene is used in dashboards, teleprinters, faxes, telex machines, TV and video chases, heat exchangers etc.

MOLECULAR WEIGHT OF POLYMERS : -

Molecular weight of polymers play an important role in deciding the physical properties of the polymers. As such physical properties of the polymers are affected by several factors. Among them the molecular weight is of great significance. The molecular weight of the polymer depends upon the number of monomer units or the repeatative units in a chain deciding the degree of polymerisation. Degree of polymerisation tells the number of monomers present in a chain. Polymer reactions are not controllable for synthesising a polymer of definite molecular weight. The molecular weight of a polymer is always found to be in a specific range. Therefore, the molecular weight and degree of polymerisation for a polymer have always been described as the average molecular weight and the average degree of polymerisation.

To explain average molecular weight, consider a sample of polymer. It contains several polymer chains. Each polymer chain represents a single polymer molecule. The number of monomer in each polymer chain is not same for polymer molecules. Therefore, a given sample of polymer, consists large number of polymer molecules with different molecular weight. So, polymer may be considered as a mixture of polymer molecules which have same chemical properties but different molecular weight. Since, molecular weight is not fixed; therefore the concept of average molecular weight has been put. There are different ways of determining the average molecular weight of polymer. They are

1) Number average molecular weight ($\overline{M}_n$)

2) Weight average molecular weight ($\overline{M}_w$)

1) Number average molecular weight :-

It is the ratio of total weight of polymer and total number of polymer molecule in sample. If ni is the number of molecules having molecular weight Mi, then number average molecular weight is given by

$$\overline{M}_n = \frac{\Sigma\, ni\ mi}{ni}$$

2) Weight average molecular weight :-

Weight average molecular weight gives the contribution of weight of each polymer molecule to the total molecular mass. If ni is the number of molecules having molecular weight Mi then weight average molecular weight is given by

$$\overline{M}_w = \frac{\Sigma\ ni\ Mi^2}{ni\ Mi}$$

It is known that the size of polymer molecule depends on the number of repeat units it contains. This number of repeat units is known as a degree of polymerisation. Similar to molecular weight, the degree of polymerisation can be averaged as number average $\overline{D}_n$ and weight average $\overline{D}_w$. These can be defined in the same way as average molecular weight. The relation between the molecular weight and degree of polymerisation, m, can be given by

$$\overline{M}_n = (\overline{D}_n)\ m$$

$$\overline{M}_w = (\overline{D}_w)\ m$$

COUMARINS : -

The fusion of a pyrone ring with a benzene nucleus gives rise to separate class of heterocyclic compounds known as benzopyrones [10]. The benzopyrones are of two distinct types, namely benzo - ∝- pyrones and benzo - γ - pyrones. They are commonly known as coumarins and chromones. (fig 3.1.).

Representative of these groups of coumarins are found to occur in the vegetable assemblage, either in the free or in the combined state. Coumarin, the simplest member of the benzo - ∝ - pyrone group, is sweet smelling constituent of wood ruff, the tonkabean and the freshly mown hay. Several coumarin derivatives have been found to be widely distributed in the plant kingdom, particularly in the plants belonging to the class of orchidacese, Leguminocease, Rutaceac Umbellifereac and Labiatac.

The coumarin ring system can give derivatives with substituents in either the benzoid part or the heterocyclic part of the molecule. This can be realized by starting a suitable phenolic compound and building up the ∝ - pyrone ring by one of the many methods available so as the synthesize the coumarin derivatives.

Coumarins have been subjected to various reactions such as bromination, nitration, formylation etc. Reactions of coumarins are discussed by Sethna and Phadke [11].

DERIVATIVES OF COUMARIN : -

Coumarin, scopoletion, Aesculetin, Ayapinfraxetine and Diaphenetin are few of the simple coumarins found in nature (Fig.3.2.)

Another interesting group of naturally occurring coumarin derivatives [12], the flurocoumarins, Psoralene, Angecilin, Bergapeth, Xamthotoxin, Pimpenellin oxeoselone and other few members (Fig.3.3).

The interest in the coumarin derivatives has increased considerably in recent years because of discovery of their varied biochemical properties, industrial uses and analytical applications.

Many natural coumarins affect the living cell of plants and animals in various ways, coumarin, itself, inhibits the germination and subsequent root growth of plants.

There is also a good probability that coumarin act as growth regulators in a number of plants

Coumarins have interesting cytogenetic properties; the microstructural effects of coumarin and its derivatives have already been studied [13]. Coumarin acts as a narcotics for some animals and as a sediative and hypnotic for the mice.

REACTIVITY OF COUMARINS :-

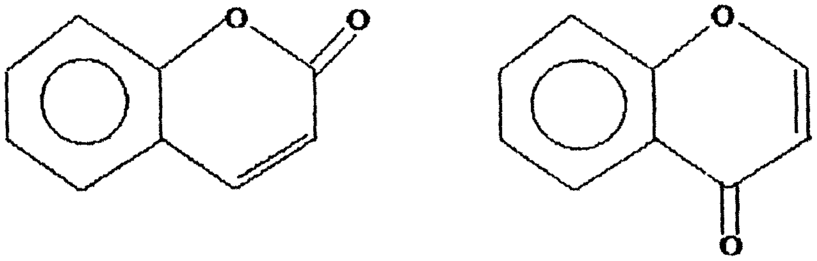
Thakar and Shah [14,15] gave the explanations of reactivity of various positions in coumarins and also the influence of various substituents in the coumarin ring in terms of the electron theory.

According to them, in coumarin their are severals systems at work simultaneously. The anionoid 'O' at 1, the cationoid 'C=O' at 2 and the system of conjugated double bonds help the electron drifts considerably (figure 3.4).

The 'O' of 'C=O' being cationoid, will cause electron displacement towards itself from the anionoid ' O ' at 1 and from position 3, which being with the double is also anionoid consequently. The reactivity of 'C=O' will be neutralized. While, the 'O'at 1 and double between 3 and 4 will partly lose their anionoid character. The 'O' at 1, being anionoid, will cause electron drifts as shown by the arrows in the figure 3.4. Thus, position 6 and 8 will be more reactive because position 8 is closer to 'O' at 1. In hydroxycoumarin the 'O' of 'OH' exerts a dominating influence.

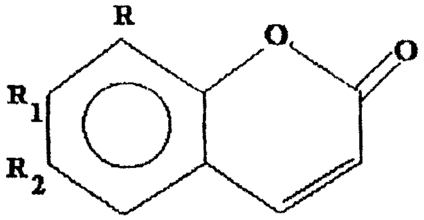
In 8 - hydroxyl coumarin, they anionoid 'O' causes electron displacement and renders position 7 reactive, position 5 also becomes reactive. While reactivity of position 6 is subdued. In 7 - OH coumarin, the 8 position is most reactive, while position 6 will also show some reactivity. Groups like Me, NH, OH etc. by exerting a negative inductive effect, increase the electron availability in all parts of the molecule. Such groups in crease speed of substitution. Groups such as NO, CN, COOH etc. which exerts a positive inductive effect, decrease the electron availability of molecule and the subtitution of more difficult

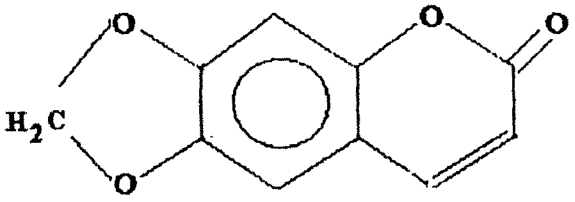
From the foregoing discussion, it will be clear that their is no single factor which determines the position of the incoming group but it is governed by several factors, the influence of double bond, - ortho and - para directing influence of hydroxyl group and the steric effect of the other group present therein.



COUMARIN **CHROMONE**

FIGURE 3. 1

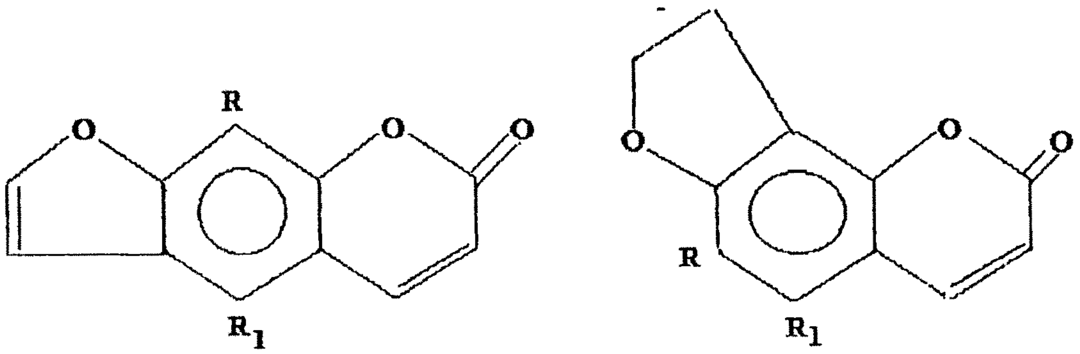




AYAPIN

	R	R$_1$	R$_2$
COUMARIN	H	H	H
SCOPOLETIN	H	OH	OCH_3
ASSCULETIN	H	OH	OH
FRAXETIN	OH	OH	OCH_3
DAPHNETIN	OH	OH	H

FIGURE 3.2



	R	R_1
PSORALENE	**H**	**H**
XAMTHOTOXIN	**OCH_3**	**H**
BERGAPTEN	**H**	**OCH_3**
ISOPIMPENELLIN	**OCH_3**	**OCH_3**

	R	R_1
ANGELICIN	**H**	**H**
PIMPENELLIN	**OCH_3**	**OCH_3**

FIGURE 3. 3

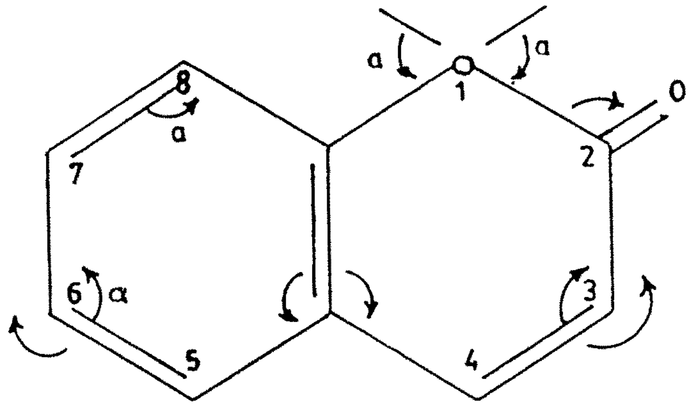


FIGURE 3.4 RING STRUCTURE OF COUMARIN

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