CHAPTER - 3

POLYMERS

INTRODUCTION

A polymer is defined as a large molecule built up, by the repeatation of small, simple units, which are joined by chemical bonds. The repeating units is known as monomer, from which the polymer is formed. There may be hundreds, thousands 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 degree of Polymerization. The molecular weight of the polymer will be the product of molecuar weight of monomer and Degree of Polymerization.

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

CLASSIFICATION OF POLYMERS

Polymer is the generic name given to vast number of materials of high moleculer weight. These materials exist in countless forms and numbers due to various types of atoms present in the molecules. There is considerable confusion concerning the classification of the polymers. Polymers have different chemical structure, physical properties, mechanical behaviour, thermal characteristics etc. Depending on these properties polymers can be classified in 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 materials are called natural polymers. Typical examples are Cotton, Silk, Wool, rubber, cellophone, cellulose, rayon RNA, DNA, etc. Polymers synthesised from compounds with low molecular weight are called Synthetic Polymers. Typical examples are polyethylene, PVC, Nylon,Terylene, PUF, Polyamide etc.

(2) Organic and Inorganic Polymers

A polymer chain essentially made of carbon atoms 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. In fact, the number and variety of organic polymers are so large that when we refer to 'polymers' we normally mean organic polymers. The polymer whose backbone chain generally contains no carbon atoms is termed as an inorganic polymer. Silicone rubber, polysilicates, polysiloxanes 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. 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 are phenolformaldehyde resins, epoxy resins, vulcanised rubber and any highly cross linked polymers.

(4) Plastics, Elastomers, fibers and liquid resins

Depending on its form and use, polymers can also be classified as Plastic, Elastomer, Fiber and Liquid resins. When polymer is shaped into hard and tough utility articles by application of heat or pressure, they are called as Plastics. Examples are polyethylene, polystyrene, PVC and PMMA.

Polymer which can be converted into elastic material having good strength and elongation, are called as Elastomers eg. natural and synthetic rubber, silicone, etc.

Polymers which can be extruded into a thin, filament like materials, are called as fiber, nylon, and terylene are the examples.

Certain polymers could be dissolved into solvent and be used as adhesives or sealant. These polymers are called Liquid resins. Examples are Epoxy adhesive and Polysulphide sealents.

(5) Isotactic, Syndiotactic and Atactic Polymers

Depending on attachment of group to the backbone chain of polymer i.e. relative geometrical arrangement groups, the polymer can be classified as Isotactic Syndiotactic, 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 groups are arranged regularly on alternate sides of the chain are known as Syndiotactic polymers.

While the polymers in which side groups are attached randomly on both sides of the chain are known as Atactic polymers.

(6) Homopolymers and Copolymers

A polymer 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 Copolymer.

Further, Copolymers are classified as Random copolymer, Alternating copolymer. Block copolymers and Graft copolymers.

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

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

When a main chain is made up of only one monomer and branches are made of other monomers attached to the main chain, the polymers are called Graft copolymers.

(7) Photoresponsive Polymers

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

TECHNIQUES OF POLYMERIZATION

Polymerization can be carried out in all three phases viz. gas phase,liquid phase and the solid phase. The liquid phase polymerization is the most commanly 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 ingradients 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 heterogenous as polymerisation. Different techniques employed for synthesis of a polymer are described below.

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

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 expoure or adding initiators. Once the polymerisation starts, the reaction mixture heats itself and reaction proceeds automatically with the increase in conversion of monomers to polymers, viscosity of the mixture increases, conversion becomes more and more difficult. Therefore, bulk polymerstion with large amount of monomers becomes explosive due to increase in temperature. The difficulty in heat removal is the main reason why few bulk polymerisation are carried in industry. 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.

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 where 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.

PRECIPITATION POLYMERIZATION

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 polymerization first as Gel particles and then become white, more or less a fine powder precipitation occurs when one reaches a certain concentration of polymers.

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 aqueous phase, in the form of small spheres of 0.1-1 mm diameter. By the addition of catalysts and by heating, polymerization can be started in few hours, the monomer droplets become highly viscous and sticky and the whole mass coagulates into a gel like precipitate, which can continue to polymerize. Mass coagulation is observed because it becomes more difficult to 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.

EMULSION POLYMERISATION

In Emulsion polymerisation, the liquid monomer is dispersed in a liquid with which it does not mix, to form 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.

INTERFACIAL POLYCONDENSATIONS

Polyesters and polyamides are usually prepared by the reaction of glycol and diamine with carboxylic acid. If one uses acid chloride, then polymerization 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 polyamide 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 polymer formed could be wrapped on rod or roller continuously. When solution becomes dilute, the thread breaks, with an exception of the polycarbonate synthesis. No industrial use has been made of this technique.

SOLID PHASE POLYMERISATION

Many monomers are capable of polymerizing not-only in the liquid phase but also in the crystalline state, below their melting points. Such polymerisation is initiated by irradiating the monomer by high energy particles. The crystal latice of a monomer may affect the rate of chain propogation, 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 polymerization of the same monomer in liquid phase.

APPLICATION 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, ceramics in the wdie variety of industries including packing, consumer products, automobiles, building 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 polycylic aromatic hydrocarbon 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 revolutionised the industry. Artificial skin, Artificial RBC, Artificial liver, Artificial kidney, lung membranes 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 used a matrix material for primary and secondary fiber reinforced composite structures. Resins also used as adhesives and sealents. Missile 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 rifle, machine gun etc. Important applications of polymers in the navy are in construction of life boats, pleasure crafts, boat hulls, propellers shafts, thermal insulation, gaskets, acoustically transparent and absorbing materials.

Blends of polyolefins are used in automobile industry for bumper coverings, wheel bearings, mud flaps dashboard stearing wheel coverings, door pockets, radiator grills etc. Other field of applications include the shoe industry, sanitory and installation engineering, sports equipments, bags and suitcases. Polyvinylchloride is used for profile the manufacture of window, guttering and street direction signs, gas pipes, cladding pannels, 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 chasis, heat exchangers.

MOLECULAR WEIGHT OF POLYMER

Molecular weight of polymer play an important role in deciding the physical properties of the polymer. 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 polymerization. Degree of polymerization 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 monomers in each polymer chain is not same for polymer molecules. Therefore, for 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 ($\bar{M}n$)
2) Weight average molecular weight ($\bar{M}w$)

1) Number average molecular weight

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

$$\bar{M}_n = \frac{\sum n.M_i}{\sum n_i}$$

2) Weight average molecular weight

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

$$\bar{M}w = \frac{\sum niMi^2}{\sum niMi}$$

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 a degree of polymerisation. Similar to molecular weight , the degree of polymerisation can be averaged as number average $\bar{D}n$ and weight average $\bar{D}w$. These can be defined in the same way as average molecular weight. The relation betwen the molecular weight and degree of polymerisation can be given by

$\bar{M}n = (\bar{D}n)\ m$

$\bar{M}w = (\bar{D}w)\ m$

EFFECT OF TEMPERATURE

If the temperature of low molecular weight compounds is increased,the solids are converted to liquids and liquids to gases. In short, we can say low molecular weight compounds exist in three states : solid, liquid and gas. But polymers exist only in the solid and liquid states. They are never in the gaseous state, as they decompose before they reach their boiling points.

If the temperature of a polymer chain is increased, localised units (Chain Segment) within the long chain molecule are first mobilised. It is possible that considerable localised motion may be observed in some part of molecule, but not in other parts due to the onset of molecular mobility. So, the molecule as a whole, does not move although some of its parts may be mobilised. Further increase in temperature leads to onset of motion of a chain as a whole, So, there are two types of motions exhibited within a polymer material namely (a) localised mobility of the chain segment, called segmental motion and (b) the mobility of a polymer molecule as a whole, called the molecular motion. The motion described by chain segments is also called as internal or microbrownian movement(10). The molecular motion described by the whole molecule is also called external or macrobrownian movement(10).

In the polymer, there is such an intermediate stage when microbrownian movement is activated but macrobrownian movement remains inactive. If the polymer is heated upto certain temperature, is rapidly cooled to the room temperature suddenly, then the chains don't get enough time to orient. This gives rise to random placing of chain segments where molecular mobility is arrested and chains are firmly held by intermolecular forces. In this, the amorphousness of the polymeric material also increases.

EFFECT OF RADIATION

When a polymer is subjected to radiation, it loses its original strength and the degradation of polymer takes place(11).

The radiation effect on a polymer can be measured by comparing relative elongation at break for different doses. Degradation is more in the exposure of long term radiation. From the study of radiation effects on polymer, radiation resistance can be evaluated(12). K. Yoshida et al(13) have tested polymer cables for their quality to withstand the radiation dose and temperature. They also observed that polymer cables can have more radiation resistance than a film of the same material. Polyimide was found to show good radiation resistance when irradiated by electron beam(11).

EFFECT OF MECHANICAL TREATMENT

When a polymer is subjected to mechanical deformation the bonds in the susceptible regions cleave. The net effect is that a big molecule is broken into small parts. Thus a polymer can be degraded by mechanical treatment. It is hard to distinguish(14) the molecular mechanism of mechanical degradation from that of thermal degradation. It can be assumed(15) that chain breaking occurs as a result of local overheating from kinetic energy ,which has been imposed on the molecule through the application of force. A. Tager(15) suggested that when a polymer is subjected to mechanical action usually degradation starts with cracks.

COUMARINS

The fusion of a pyrone ring with a benzene nucleus gives rise to separate class of heterocyclic compounds known as benzopyrones(16). The benzopyrones are of two distinct types, narmely benzo α-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- α - 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 kindgom, particularly in the plants belonging to the orders of Orchidaceae, Leguminoceac, 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 α-pyrone ring by one of the many methods available so as to synthesize the coumarin derivatives.

Coumarins have been subjected to various reactions such as bromination, nitration, formylation etc. Reaction of Coumarins are discussed by Sethna and Phadke(17).

DERIVATIVES OF COUMARIN

Coumarin, scopoletin, Aesculetin, Ayapin fraxetine and Diaphnetin are few of the simple coumarins found in nature (fig 3.2).

Another interesting group of naturally occuring coumarin derivatives(18), the fluorocoumarins, Psoralene, Angecilin, Bergapten, Xamthotoxin, Pimpenellin oxeoselone are 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 microstructural effects of coumarin and its derivatives have already been studied(19).

Coumarin acts as narcotics for some animals and as a sedative and hypnotic for the mice.

REACTIVITY OF COUMARIN

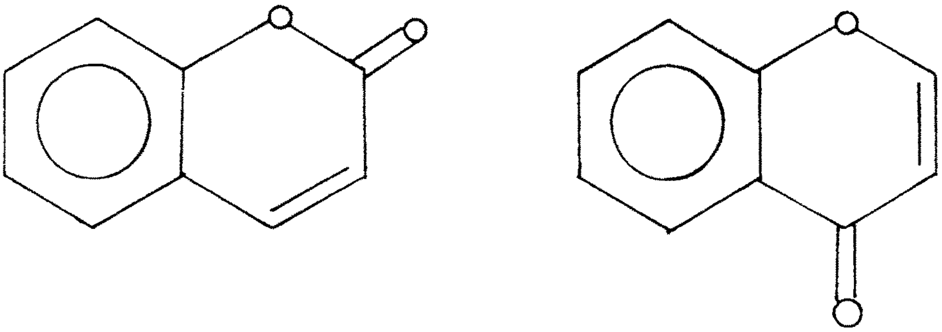
Thakar and Shah(20,21) gave the explanations of reactivity of various positions in coumarin and also the influence of various substituents in the coumarin ring in terms of the electron theory.

According to them, in coumarin there are several systems at work simultaneously. The anionoid 'O' at 1 the cateonoid 'C = O' at 2 and the system of conjugated double bonds help the electron drifts considerabley (fig.3. 4).

The 'O' of 'C = O' being cationoid, will cause electron displacement toward itself from the anionoid 'O' at 1 and from position 3, which having a double bond is anionoid Consequently, the reactivity of 'C = O' will be neutralised. While, the 'O' at 1 and double bond between 3 and 4 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 hydroxy coumarins the 'O' of 'OH' exerts a dominating influence.

In 8-hydroxy coumarin, the anionoid 'O' causes electron displacement and renders position 7 reactive, positon 5 also becomes reactive. While reactivity of position 6 is subdued. In 7-OH coumarin, the 8 position is most reactive, while position 6 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 increase the speed of substitution. Groups such as NO , CN, COOH etc. which exert a positive inductive effect, decrease the electron availability of molecule substitution more difficult.

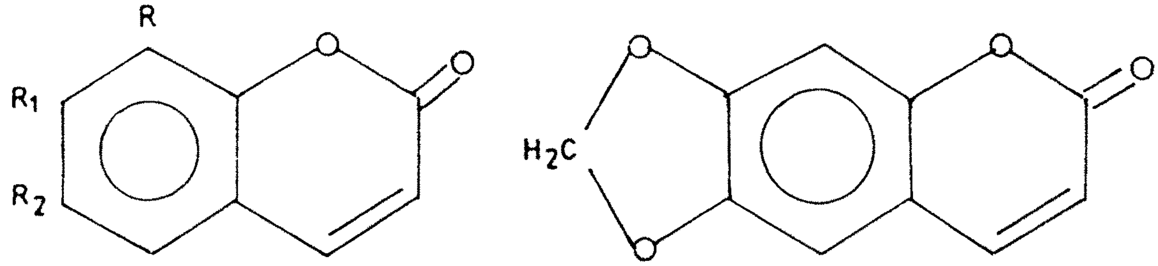
From the foregoing discussion, it will be clear that there is no single factor which determines the position of the incoming group but it is governed by several factors, the influence of double bond, the ortho and para directing influence of the hydroxyl groups and steric effect of the groups present.



COUMARIN

CHROMONE

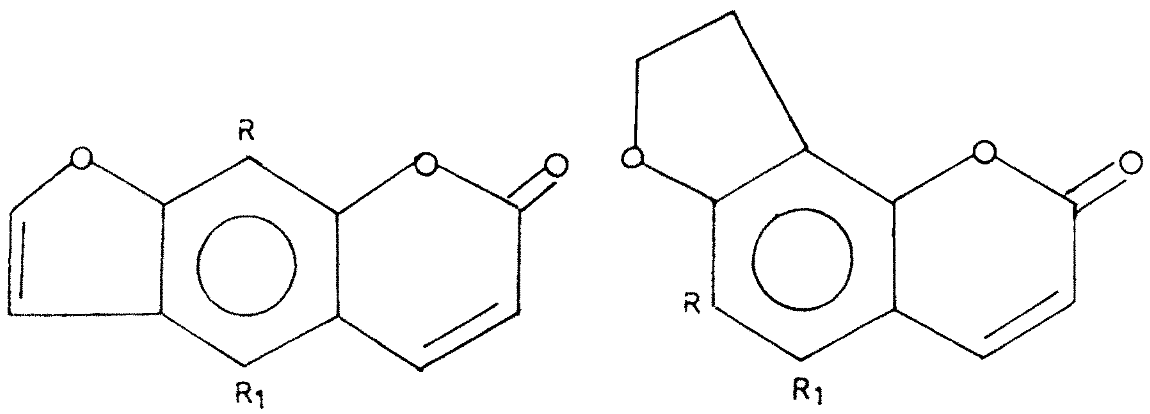
FIG. 3-1



AYAPIN

	R	R_1	R_2
COUMARIN	H	H	H
SCOPOLETIN	H	OH	OCH_3
AESCULETIN	H	OH	OH
FRAXETIN	OH	OH	OCH_3
DAPHNETIN	OH	OH	H

FIG. 3-2



	R	R1
PSORALENE	H	H
XANTHOTOXIN	OCH_3	H
BERGAPTEN	H	OCH_3
ISOPIMPINELLIN	OCH_3	OCH_3

	R	R1
ANGELICIN	H	H
PIMPINELLIN	OCH_3	OCH_3

FIG 3-3

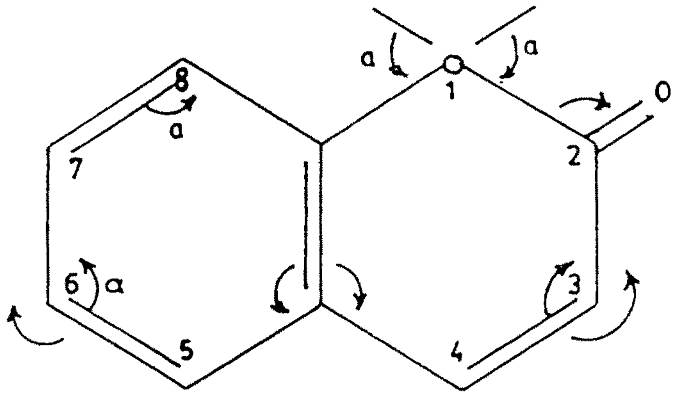


FIG. 3-4 RING STRUCTURE OF COUMARIN

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