CHAPTER - III

POLYMERS

A. INTRODUCTION

In everyday life, we come across a large number of objects made out of plastics, rubber, fibres, foam and a variety of such things. These are objects said to have been made up of 'polymers'. 'Polymer' is a word from Greek language, meaning many units or parts. (Poly: many and mer : unit or part). In general a non-metallic material consisting of a large macromolecules composed of many repeating units can be called a polymer.

Since ancient times, naturally occuring polymers have been used by mankind for various purposes. Proteins from meat and polysaccharides from grains form important sources. Wool and silk, both proteins, serve as clothing material. Wood, the main component of which is cellulose i.e. a polysaccharide is used for building and fire-making. Amber, a high-molar mass resin, was worn by the Greeks as jewel. The use of asphalt as an adhesive is mentioned in the Bible.

(i) Brief History

In the early part of this century organic chemists were still confining their attention to the compounds, which could readily be distilled or crystallized. When substances were encountered that could not be purified by conventional procedures, they were promptly thrown away. Many of these discarded materials were polymers, which in those days were assumed to be impure aggregates of small molecules held together by colloidal forces. Although it may seem odd now, this concept was well entrenched when Staudinger[1] proposed that rubber and other polymers were actually composed of giant molecules, he called them the macromolecules. At first, virtually no one agreed with him. In fact, his hypothesis met with stubborn criticism all through the next decade. Meanwhile, bits of evidence corroborating the macromolecular theory began to accumulate from X-ray studies, molecular weight measurements and similar sources. After 1930, even the most persistent doubts faded away rapidly with the introduction of numerous new polymers that gradually revolutionized the plastics, textiles, rubber and other related inustries.

With the exception of Staudinger's studies[2,3], nearly all pioneering work on synthetic macromolecules was done in industrial laboratories. But as the academic interest grew, research turned towards the natural polymers that form food, clothing and shelter as well as the basic structures and functions of all the living things.

(ii) Polymerization

Polymers are macromolecules built up by linking together of large number of many smaller molecules. The small molecules that combine with each other to form polymer molecules are termed monomers, and the reaction by which they combine are termed polymerization. There can be hundreds, thousands, tens of thousands or more monomer molecules linked together in a polymer molecule. When one speaks of polymers, one is concerned with materials whose molecular weights may reach into the millions.

(B) CLASSIFICATION OF POLYMERS

There has been and still is considerable confusion concerning the classification of the polymers. During the development of polymer science, two types of classifications of polymers have come into use. One classification divides polymers into condensation and addition polymers and the other divides them into step and chain polymers. Confusion and error arise because the two classifications are usually used interchangeably without careful thought. The terms condensation and step are usually used synonymously as are the terms addition and chain. Although these terms can often be used synonymously as noted, this is not always the case because the two classifications arise from two different bases. The condensation-addition classification is primarily applicable to the composition or structure of polymers. The step-chain classification is based on the mechanism of polymerization reactions.

(i) Composition and Structure

Polymers were originally classified by Carothers[4] in 1929 into condensation and addition polymers on the basis of the compositional difference between the polymer and monomer from which they were synthesized. Condensation polymers were those polymers formed from polyfunctional monomers by the various condensation reactions of organic chemistry with the elimination of some molecules such as water. Some naturally occuring polymers such as Cellulose, Starch, Wool and Silk are classified as condensation polymers. Addition polymers were classified by Carothers as those formed from monomers without the loss of a small molecule. Unlike condensation polymers, the repeating unit of an addition polymer has the same composition as the monomer. The major addition polymers are those formed by polymerization of monomers containing the carbon-carbon double bond.

(ii) Mechanism

Polymerization is the reaction of linking together of several molecules (monomers), not accompanied by the formation of by products and involving no change in elementary composition.[5]

Since the polymeric state, in which the monomer residues are tied together into long chains is always less probable than the state of a completely disordered mixture of the monomer molecules, the formation reaction is possible only because it corresponds to the transition of an energy-rich to an enery-poor state and because all formation reactions of macromolecules are exothermal.

The magnitude of the heat of reaction can be quite different with the different reactions which lead to macromolecules.

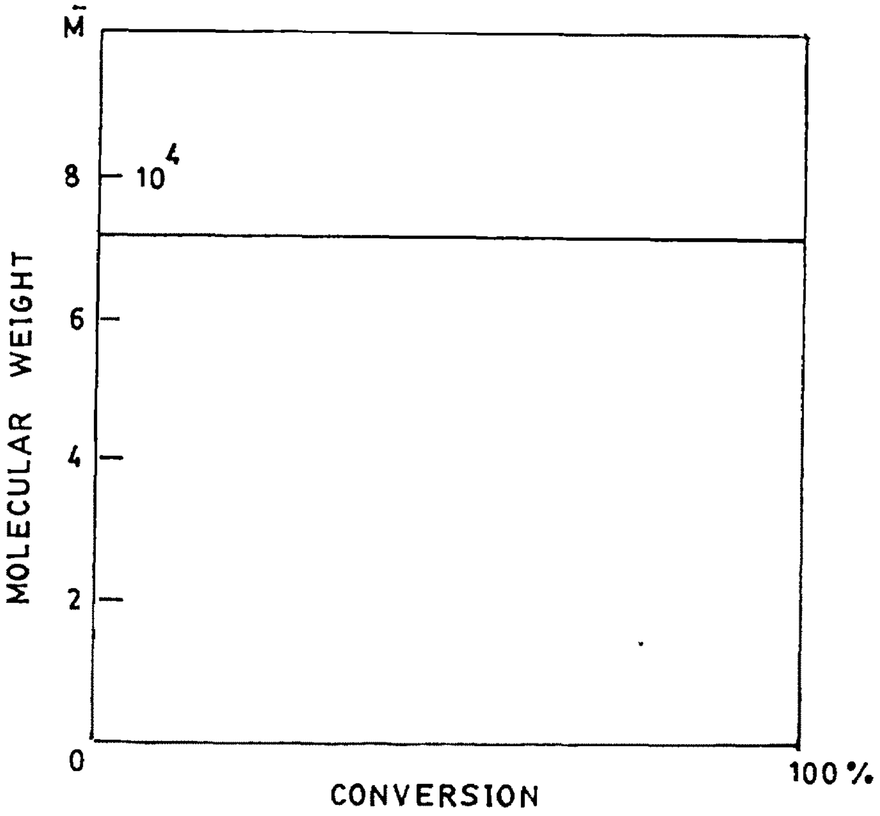


FIG. III - 1

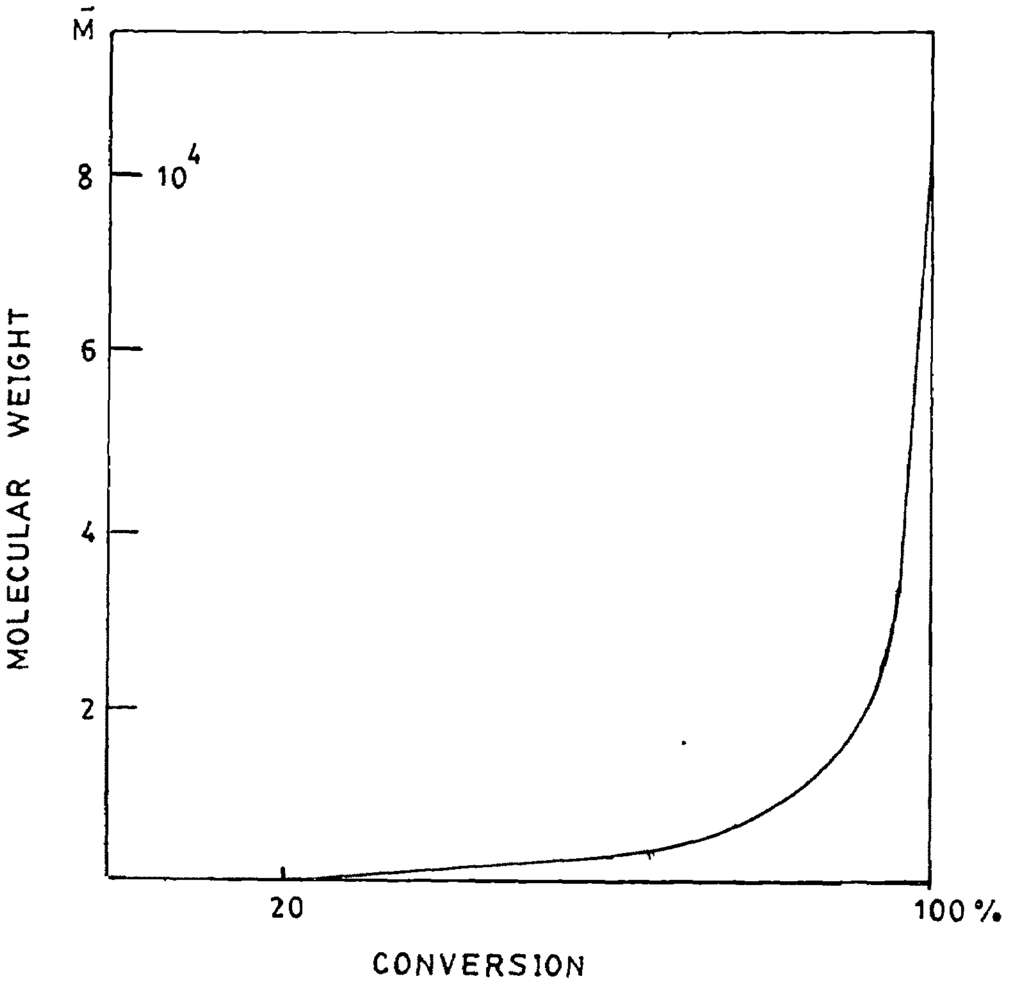


FIG. III - 2

In theory, all reactions, that lead to the formation of macromolecules are equilibrium reactions. The polymerization is affected by temperature. The higher the temperature, the greater is the concentration of monomer, which is in an equilibrium state. The lower the temperature, the concentration of the polymer in the equilibrium increases. With the selection of a suitable initiator it is possible to bring about reversible, polymerization and depolymerization.

If water or other small molecules are formed in the preparation of a polymer, as for example in the formation of polyester from glycols and dicarboxylic acid, the equilibrium depends not only on the temperature but also on the concentration of water. To obtain polymers of a high molecular weight through polycondensation reactions one must remove the water carefully from the equilibrium. In the same way excess of acid, amide or alcohol affects the equilibrium. One obtains macromolecules with two amino, or two carboxyl or two alcohol end groups which cannot find a reaction partner, and therefore, a further increase in molecular weight becomes impossible. It is very difficult to obtain macromolecular compounds with high molecular weights through polycondensation reactions, because the removal of last traces of water in the reaction mixture is coupled with a number of technical difficulties. This is why industrially produced polycondensates such as polyamides and polyester have molecular weights of about 20,000 whereas commercial addition polymers usually have molecular weights of the order of 200,000.

The fact that a polymerization (or a polycondensation or polyaddition) is thermodynamically possible; does not mean that it can occur with a useful reaction velocity, even at normal temperatures. In most cases, one has to use higher temperatures or a catalyst to overcome the potential barrier which prevents the transition, from monomer to polymer.

The many reactions used for the preparation of linear macromolecules can be subdivided into two main groups which differ from each other completely in their kinetics :

(1) Polymerization of unsaturated olefin monomers or cyclic monomers by a chain reaction.

Initiater $\xrightarrow{\text{Decomposition}}$ 2 Radicals R.

Radical R. + Monomer M $\longrightarrow$ R - M. (Initiation)

R - M. + M $\longrightarrow$ R - M - M.

Chain radical R$\sim$M. (Propagation)

R$\sim$M. + M$\sim$R $\longrightarrow$ R$\sim$M - M$\sim$R (Termination)

Depending on the type of initiation, one can differentiate between radical, ionic or metal complex polymerizations. Unsaturated compounds of the type of ethylene and its derivatives, but also such cyclic monomers as ethyleneoxide or trioxane are easily polymerized according to the above scheme. Of the compounds with (C=O) double bonds, only formaldehyde leads to relatively stable polymers. Other compounds with

CO group (e.g. aceltaldehyde acetone) together with ethylene have also been polymerized, but the resulting polymers are highly thermally unstable for any important industrial applications.

(2) **Polymerization by stepwise reaction of monomers with functional groups.**

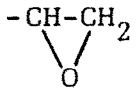
(a)
$$O - O + X - X \rightleftharpoons O - \otimes - X$$
$$O - \otimes - X + O - O \rightleftharpoons - \otimes - \otimes - X$$
$$O - \otimes - \otimes - O + X - X \rightleftharpoons O - \otimes - \otimes - \otimes - X$$
$$O - \otimes - \otimes - \otimes - X + O - \otimes - \otimes - \otimes - X \rightleftharpoons O - \otimes - \otimes - \otimes - \otimes - \otimes - \otimes - X \text{ etc.}$$

(b)
$$O - X + O - X \rightleftharpoons O - \otimes - X$$
$$O - \otimes - X + O - X \rightleftharpoons O - \otimes - \otimes - X \text{ etc.}$$

(c)
$$\otimes \rightleftharpoons O - X$$
$$O - X + \otimes \rightleftharpoons O - \otimes - X$$
$$O - \otimes - X + \otimes \rightleftharpoons O - \otimes - \otimes - X \quad \text{etc.}$$

O and X are functional groups which can react with each other to form x, a homopolar main valence bond.

For examples :

O		X	O		X
$-OH$	+	$-COOH$	$-NH_2$	+	$-COOH$
$-OH$	+	$COCl$	$-NH_2$	+	$-N=C=O$
$-OH$	+	$-N=C=O$	$-NH_2$	+	$COOCH_3$
$-OH$	+				

The two different groups, O and X may be as shown in reaction 2(a), distributed over two different monomer molecules (for example, adipic acid and hexamethylene, diamine 6,6 Nylon). However, they can also be in one and the same monomer molecule (for example with w - amino acid) or they can form a ring in which two groups are then present within the ring in a condensed form (for example caprolactum ⟶ 6, nylon).

The following are the basic differences between the two types of polymer forming reactions.

(a) With polyaddition

In the case of polyaddition polymerization, the monomers can react only with the relatively few radicals or ions present but not with each other. By additions of monomers at the few active centres the chain molecules grow rapidly in a 'sudden rush', within short time span until they have reached their definitive length by chain termination. Once the growth has terminated the formed macromolecules do not participate in the polymerization reaction any more (except where chain transfer reactions occur). This type of chain growth reaction causes the length of the polymer chains to be more or less independent of the degree of conversion (Figure: III-1). Just the opposite holds for the other type of reaction II, polycondensation, which is characterized by a very strong dependence of the chain length on the degree of conversion (Figure: III-2).

(b) With polycondensation

In the case of polycondensation, all reaction patterns have the same reactivity, and no preferred reaction centre exist. Each monomer molecule can react with other monomer molecule so that at first at lower conversions below about 80% preferrably dimers, trimers and other oligomers are formed. Only at high conversion above 98-99% long chain polymers are formed. Polycondensation reactions occur in stepwise manner i.e. it is possible to interrupt the reaction (by cooling) at any time without affecting the reactivity of the present chains of oligomers or polymers. The reaction can be continued at any time (by heating) and the oligomers and polymers will continue to react with each other.[6]

(iii) Linear branched and crosslinked polymers

Polymers can be classified as linear, branched or crosslinked polymers depending on their structure. Polymers in which the monomer molecules have been linked together in one continuous length to form the polymer molecule, are termed the linear polymers.

Branched polymer molecules are these in which there are side branches of linked monomer molecules protruding from various central branch points along the main polymer chain. Branched polymers are often obtained in both step and chain polymerizations.

When polymers are produced in which the polymer molecules are linked to each other at points other than their ends, the polymers are said to be crosslinked. Crosslinking can be made to occur during the polymerization process by the use of appropriate monomers. The ability of an element to form polymeric compounds depends on its position in the Mendeleev's periodic system.

(iv) Organic, elemento-organic and in-organic polymers

Polymers may be classified as organic, elemento-organic (or hetero-organic) and inorganic. However, it is very difficult to draw sharp boundary between these three classes, because there are many different compounds intermediate between them.

Organic polymers include compounds containing, apart from carbon atoms, hydrogen, oxygen, nitrogen, sulphur and halogen atoms; even though the oxygen, nitrogen or sulphur are found to be in the backbone chain.

Organic polymers also include polymer substances containing other elements in their molecules provided the atoms of these elements are not in the main chain and are not connected directly to carbon atoms.

Elemento-organic or hetero-organic polymers include :

(a) Compounds whose chains are composed of carbon atoms and hetero-atoms (except for nitrogen, sulphur and oxygen atoms).

(b) Compounds with inorganic chains if they contain side group chain hetero-atom with carbon atoms connected directly to the chain.

(c) Compounds whose main chains consist of carbon atoms and whose side groups contain hetero-atoms connected directly to the carbon atoms of the chain.

Inorganic polymers are polymers containing no carbon atoms. Metals are not classed as polymers, because they are characterized by what is known as a metallic bond, meaning combination of ions in the crystal through free mobile electrons. Ordinary salts are not polymers either, because they possess ionic chemical bonds, salts dissociate into ions in dilute solutions.

Compounds that should be classed as inorganic polymers are those whose chains are composed of different atoms joined by chemical bonds, while weaker intermolecular forces act between the chains. The elements of group I, do not form polymeric compounds; those of group II (beryllium, cadmium etc.) form heterochain polymers.

Especially, important are the heterochain polymeric compounds of group III and group IV elements.

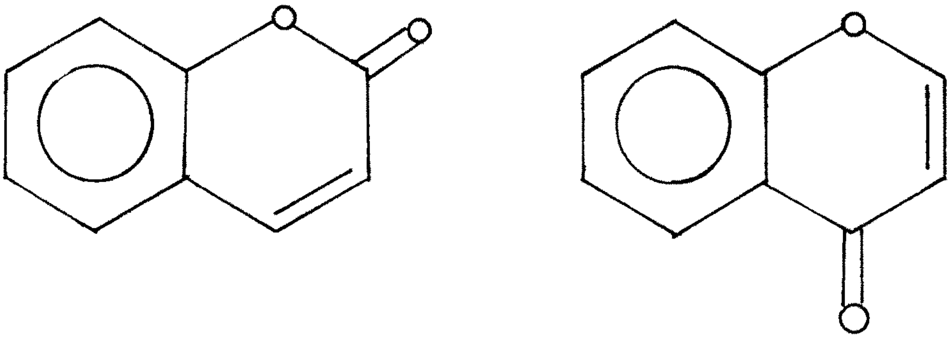
Homochain polymers of IV-VI group elements.

All the elements of group IV can form linear chains analogous to those of polyethylene.

The elements of group V usually form low-molecular compounds, but under certain conditions they can change into polymers.

White phosphorus consists of P_4 molecules arranged in the form of a tetrahedron. When heated it passes into a polymer. Red phosphorus results when the white modification is heated to 500°C. This is a less ordered form of polymeric phosphorus. The most ordered form is black phosphorus which forms from white phosphorus when the latter is heated at 200°C and 12000 atm. It is a polymeric compound with a lamellar lattice like that of graphite.

Arsenic forms an amorphous polymer when heated at comparatively low temperatures and rhombohedric crystalline polymer when heated at 270°C. Polymeric forms of antimony are known, analogous to those of red phosphorus and aresenic. Sulphur and Selenium (group VI) have a high tendency to form linear homochain polymeric



COUMARIN

CHROMONE

FIG. III - 3

compounds. Ordinary rhombohedric sulphur has cyclic molecules containing eight sulphur atoms each.

Organic polymers fall into aliphatic and aromatic ones. Depending on the nature of a substituent, each of these classes may be divided into hydrocarbons, halogen derivatives, alcohols, acids, ethers, esters, nitriles, aldehydes, ketones etc.

Aromatic polymers are now widely used, since in most cases they are heat-resistant and this is the characteristic which is very important to modern technology.

C. COUMARINS

The fusion of a pyrone ring with a benzene nucleus gives rise to a new class of heterocyclic compounds known as benzopyrones. The benzopyrones[7] are of two distinct types; namely benzo-α-pyrones and benzo-γ-pyrones. They are commonly known as coumarins and chromones, respectively (Figure III-3).

Representative of these group of compounds 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 the 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 natural orders of Orchidaceae, Leguminoceae, Rutaceae, Umbelliferaeae and Labiatae.

The coumarin ring system can give derivatives with substituents in either the benzenoid part or the heterocyclic part of the molecule. This can be realized by starting with 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, sulphonation etc..

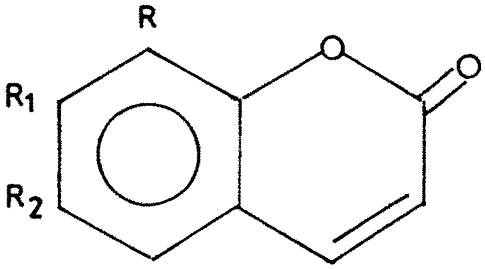
(i) Derivatives of Coumarin

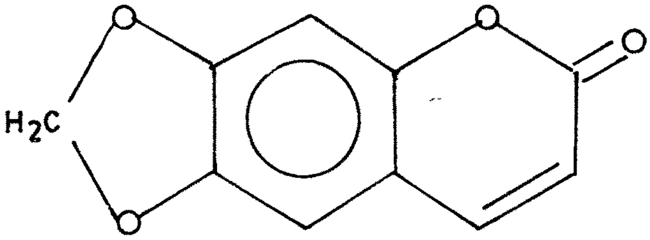
Coumarin, Scopoletin, Aesculetin, Ayapin, Fraxetin and Daphnetin are a few of the simple coumarins found in nature (Figure-III-4).

Another interesting group of naturally occuring coumarin derivatives[8]; the furocoumarins Psoralene, Angelicin, Bergapten, Xamthotoxin, Pimpenellin, Isopimpinellin and Oxeoselone are few of the members (Figure III-5).

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

Many natural coumarins affect the living cell of plants and

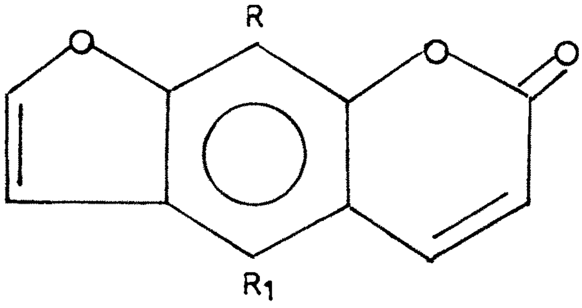




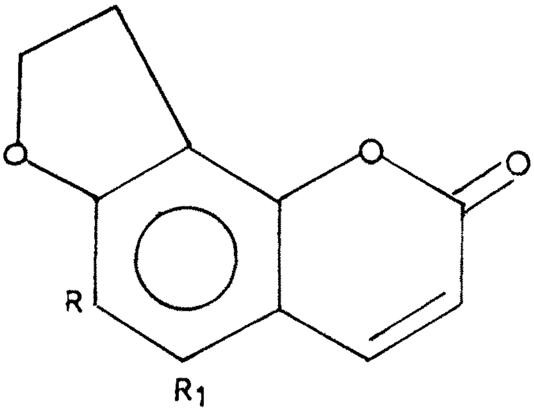
AYAPIN

	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. III 4



	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 III-5

animals in various ways. Coumarin itself, inhibits the germination and subsequent root growth of plants.

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

Coumarins have interesting cytogenetic properties. Cytohistological and microscopical effects of coumarin and its derivatives have already been studied.

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

(ii) Reactivity of Coumarin

Thakar and Shah[9], gave the explanations of the reactivity of various positions 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 cationoid C=O at 2 and the system of conjugated double bonds helps the electron drifts considerably (Figure III-6).

The O of C=O being cationoid, will cause electron displacement towards itself from the anionoid O at 1 and from position 3, which having a double bond is anionoid. Consequently, the reactivity of

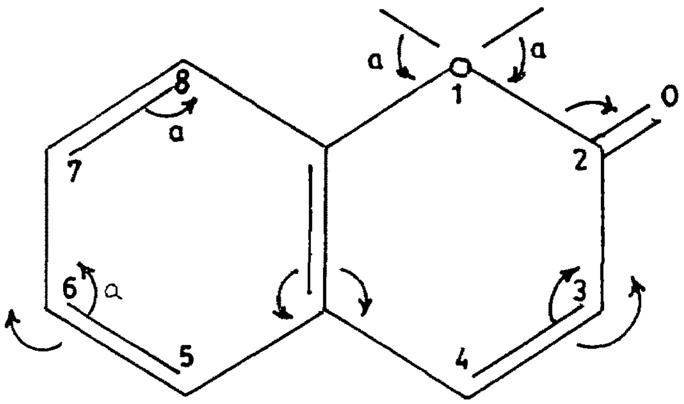
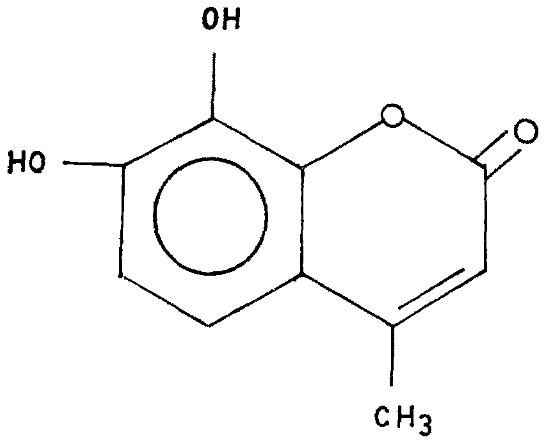


FIG. III-6 RING STRUCTURE OF COUMARIN

C=O will be nullfied while both, the O (at 1) and the 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 marked ${}_{a}\curvearrowleft\ \curvearrowright^{a}$ in the figure. Thus, position 6 and 8 will be more reactive because position 8 is closer to 0 at 1. In hydroxy coumarins the 0 of the OH exerts a dominating influence.

In 8-hydroxy coumarin, the anionoid O causes electron displacement and renders position 7 reactive, position 5 also becomes reactive, while the reactivity of position 6 is subdued. In 7-OH coumarin the 8-position is made most reactive, while position 6 will also show some reactivity. Groups like Me, NH_2, 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_2, CN, COOH etc. which exert a positive inductive effect, decrease the electron availability of the molecule making 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 the double bond, the -ortho and -para directing influence of the hydroxyl groups and the steric effect of the groups present.



7,8-DI-HYDROXY 4-METHYL COUMARIN (MONOMER)

FIG: III-7

D. PREPARATION OF MONOMER AND ITS CO-POLYMERS

The present section deals with the synthesis of dihydroxy monomers which were then subjected to the solution polycondensation.

Phthalic acid, Iso-phthalic acid, Terephthalic acid, Sebacic acid and Maleic acid were acquired from the local market and were used without further purification. The above acids were claimed to be pure to 99.9% by the manufacturers.

(i) Synthesis of Monomer

An ice-cold mixture of Ethyl-aceto-acetate and conc. H_2SO_4 was prepared. The proportionate quantity of pyrogallol was added slowly to this ice cold mixture by maintaining the temperature between 0 and 5°C. The reaction mixture was left undisturbed overnight. Next day, it was poured on the ice-cold water or on the crused ice. The solid was thus separated out, which was then filtered and dried. This is the required monomer (A) which was recrystallized from alcohol for purification M.P. 235°C (Figure III-7).

(ii) Synthesis of Polymer

The synthesis involves two steps, first step being the preparation of acid chloride and second one the polymerization.

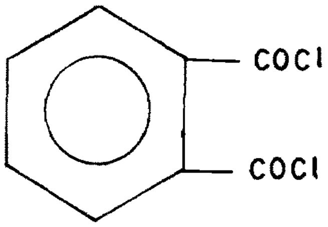
1 SEBACYL CHLORIDE

$ClOC - (CH_2)_8 - COCl$

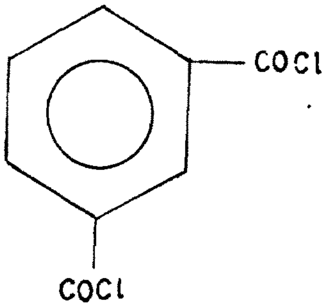
2 MALEIC ACID DI CHLORIDE

$$\begin{array}{ccc} CH & = & CH \\ | & & | \\ COCl & & COCl \end{array}$$

3 PHTHALOYL CHLORIDE



4 ISOPHTHALOYL CHLORIDE



5 TEREPHTHALOYL CHLORIDE

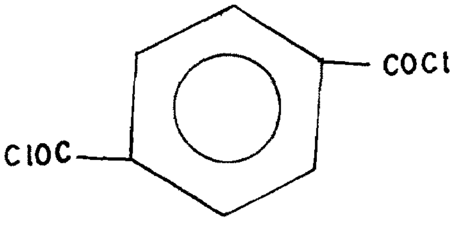


FIG. III 8 STRUCTURAL FORMULAE FOR ACID CHLORIDES

(a) Preparation of Acid Chloride

1:2 proportion of an acid and thionyl chloride was refluxed on the water bath for 3 to 4 hours. A drop or two of pyridine was added as catalyst in the preparation of acid chloride. Excess of thionyl chloride was distilled off under reduced pressure using a vacuum pump.

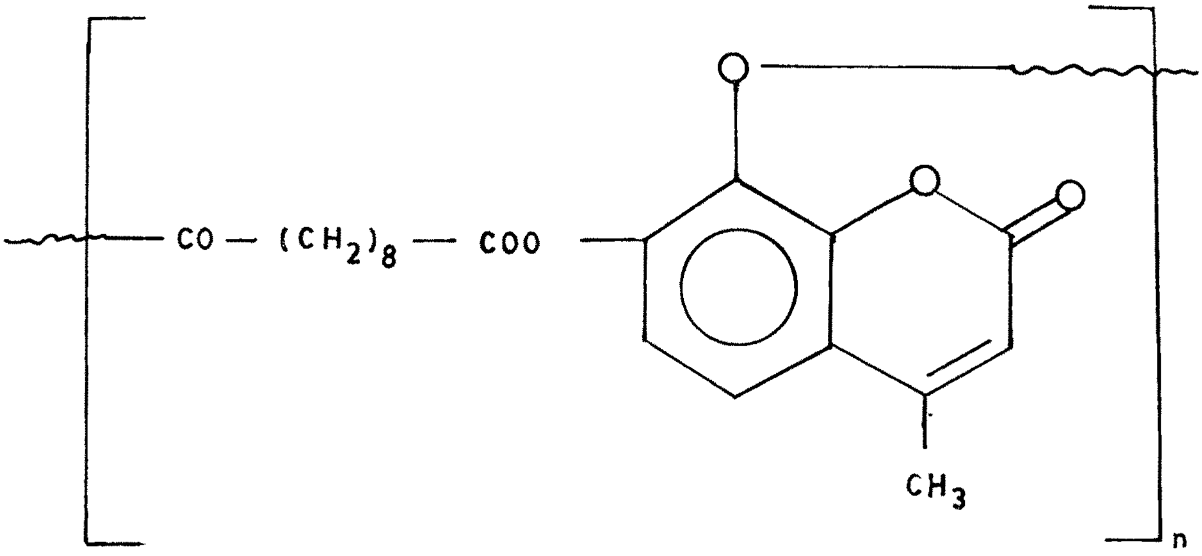
Five acid chlorides were synthesized by above method and they were used for the next step without further purification. The list of acid chloride prepared is as in Figure III-8.

(b) Polymerization

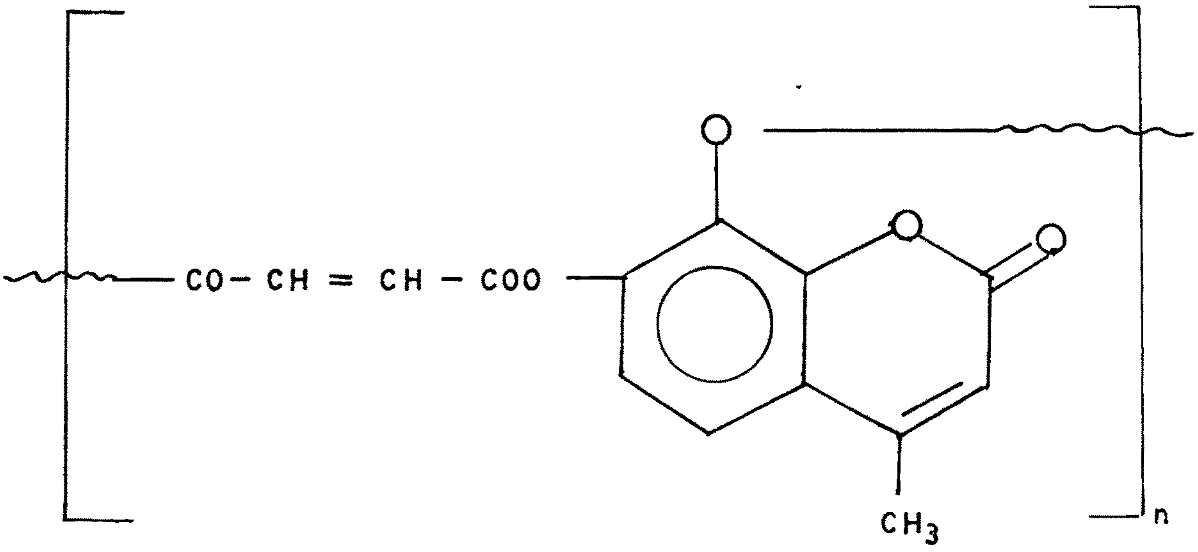
Polymers were prepared by condensing different di-acid chlorides with 7,8-dihydroxy-4-methyl coumarin monomer A.

An appropriate acid chloride was dissolved in dry pyridine and cooled in an ice bath. Then 7,8-dihydroxy-4-methyl coumarin monomer dissolved in pyridine, was added with stirring. The reaction mixture was stirred continuously for one and half hour. After the stirring period, the whole reaction mixture was decomposed in 1:1 - ice cold water : HCl solution. The white precipitate was separated, filtered and washed with alcohol.

The precipitate was purified by solvent-nonsolvent method. DMF was used as solvent and alcohol was used as non-solvent

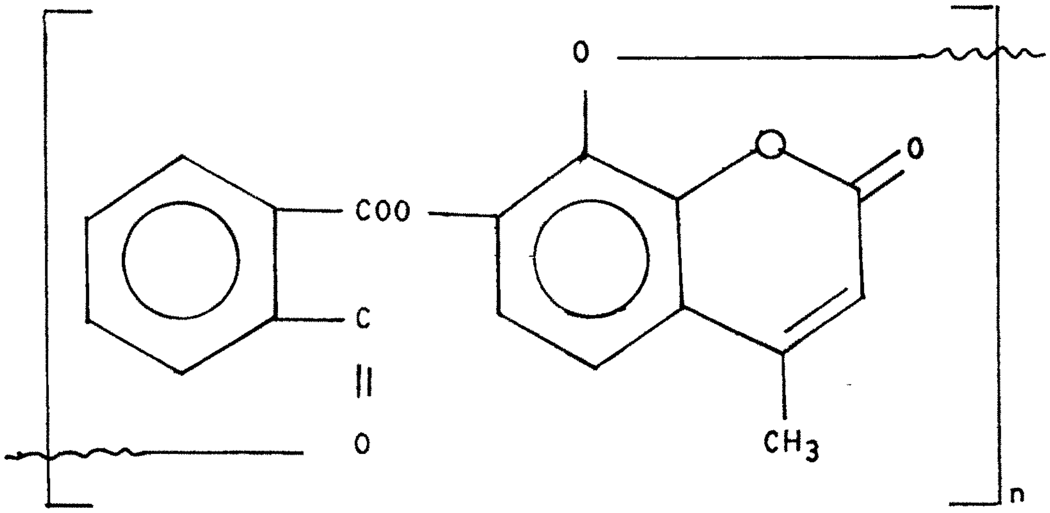


POLYMER SPECIMEN A_1

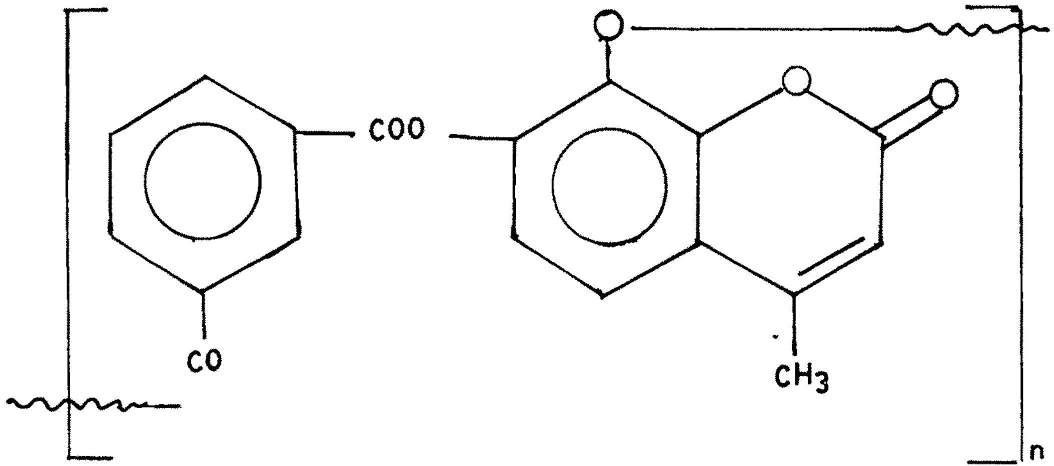


POLYMER SPECIMEN A_2

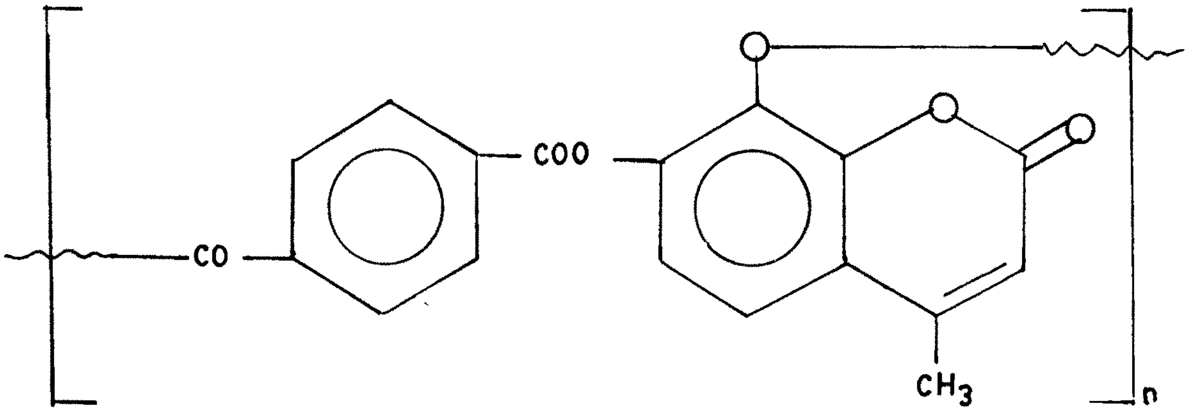
FIG III-9



POLYMER SPECIMEN A_3



POLYMER SPECIMEN A_4



POLYMER SPECIMEN A_5

in the purification process.

The structural formulae for the acid chloride have been shown in Figure III-8. The structural formulae for the polymers have been shown in Figure III-9.

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