CHAPTER I

INTRODUCTION

As early as 1667, Robert Hooke prophesied that "there might be a way of making an artificial glutinous composition, much resembling, if not full as just, nay better, than the excrement from the silk worm". This prophesy did materialise, though only in the first half of the twentieth century, due to the tremendous advances made in the field of polymer chemistry in this period. The acceptance of the hypothesis that high polymers are composed of covalent structures many times greater than that occurring in small molecules and this alone accounts for the characteristic properties which set them apart from other forms of matter is largely responsible for the rapid advances in high polymer chemistry. But unfortunately this view was not accepted by the chemists till about 1930. They considered the process of polymerisation as depending entirely on the forces of auxilary valency, which may be regarded as being either of a general nature or exerted in the form of definite co-ordinate linkage of the type described by Sidgwick. Thus Thiele[1] in 1899 suggested that in a molecule which undergoes polymerisation the affinity forces of the compound atoms are not completely satisfied and the residual affinities which he termed "partial valencies" bind the molecules to form polymers. Again in 1901 a school of chemists[1] put forward the view that polymerisation is a kind of allotropic change and not a chemical change. They considered polymerisation of acrylic ester as an allotropic change. Schorerter[1] suggested that polymerisation is a manifestation of the peripheral force and no chemical structure is involved. Thus the view that polymerisation is a type of association caused by some inter-molecular forces of mysterious origin was so strongly advocated that even the early investigators on natural as well as synthetic polymers tried to view their results only through this angle and the gradual change to the present view, that properties like viscosity, elasticity and high strengths are direct consequences of the size and constitution of covalent structures and not due to inter-molecular forces, which also do influence the properties of high polymers just as they do those of monometric compounds, may be seen from a brief review of the early investigations on naturally occurring as well as synthetic polymers.

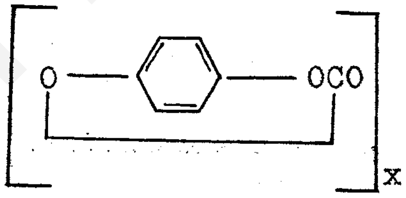
Early Investigations on Naturally Occurring Polymers

The polymeric nature of proteins and carbohydrates was recognised atleast as early as 1871 when Hlasiwetz and Habermann[2] suggested that these substances include a host of isomeric and polymeric species differing from one another with respect to molecular condensation. Thomas Graham[3] observed the slow or even negligible rates of diffusion of certain polymers in solution and their inability to pass through semi-permeable membranes. He coined the term "Colloids" meaning "glue like" for these substances. For a long time the workers in this field were handicapped by the absence of a method of determining molecular weight in solution, and hence could not determine the state of polymerisation even in instances where polymerisation was suspected. However the work of Raoult[4] and Van't Hoff's[5] formulation of solution laws provided them with a tool to determine the molecular weight. Sonn followed a period when a number of people were engaged in determination of molecular weights of starch, rubber etc. It may be mentioned here that excepting Nastukoff[6] nobody realised the importance of extrapolating the measurements to zero concentration and partly due to this the molecular weight values obtained by them are much too low. From the molecular weight determinations a few of the early investigators were led to believe that cellulose, starch etc. are composed of large molecules. This view was not accepted in general and they preferred to believe that the laws applicable to ordinary solutions are not applicable to colloids. Further the apparent deviations for solutions of electrolytes seemed to testify the fallibility of Raoult's method. Again as mentioned earlier the period 1895-1920 was marked by the emphasis placed on secondary association of molecules through coordination complexes, partial valencies and Van der Waal's forces and Ramsay and Shields[7] publication provided a method of estimating the extent of this association, by which many workers could prove that association is very common in liquids. Organic Chemists were motivated by the desire to isolate "pure" substances the term "pure" being synonymous with "homomolecular" and invariably implying a formula of convenient size. People were so absorbed with the association theory that molecular association was unfortunately referred to as polymerisation. The emphasis placed on the not infrequent occurrence of co-ordination compounds and of association in liquids sustained the view that polymeric substances are similarly physical aggregates of smaller molecules. The degradative studies on rubber, cellulose, starch etc. indicated the existence of more than one monomer unit linked by covalent linkage. These polymeric units might be combined either in cyclic structures or open chains. The assumption of a linear chain requires the presence of end groups which they could not detect. Hence it was believed that these polymers are formed by association of ring structures containing more than one unit. However Emil Fischer's[8] synthetic approach towards proteins indicated that the chains are linear, but his estimate of the length of the chain was too small by one to four orders of magnitude depending on the protein.

Early Encounters with Synthetic Resins

A) Condensation Polymers

The possibility of indefinitely large covalent structures is implicit in the basic structural concepts of organic chemistry. But the early Organic Chemists not only did not pay any attention to this but also discarded the tarry side products and insoluble products obtained when bifunctional or polyfunctional reactions were carried out[9]. In the early days of scientific development of polymer field, the orthodox organic chemist called the polymer chemist a student of "gunks" and indicated that the purity of his products was for less than that demanded in the ordinary synthetic work. Nevertheless a few of the synthetic polymeric substances did attract the attention of the 19th century investigators. Thus Lourenco (1860)[10] reported the synthesis of polyethyleneglycol. He found the viscosity of this product increased with the number of units in the chain. His remarkably clear understanding of the nature of the polymeric product may be understood from his statement "We have demonstrated that the percentage composition and even the chemical reactions are insufficient to determine the chemical molecule of certain compounds and that there should exist organic and inorganic bodies having the same apparent percentage composition, presenting the same reactions and having however entirely different degrees of condensation". Lourenco[11] also prepared polyethylene succinate. Vorlander[12] assigned to it a sixteen membered ring structure composed of two units. Roithner[13] suggested a cyclic tetrameric formula for polyethylene oxide, inspite of molecular weight measurements which indicated an empirical formula $(C_2H_4O)_{30}$. Kraut[14] on the basis of sound chemical evidence assigned chain structures to the products obtained by heating acetyl salicylic acid and also to "salicylide" obtained by action of phosphorous oxychloride on sodium salicylate. The curious notion of condensation in discrete steps from one intermediate to another of twice the degree of polymerization was advanced by these as well as later workers. Kraut, like many other early investigators believed that the polymers obtained are homogeneous and not mixtures of polymeric species. Nevertheless recognition of the essential nature of chain polymeric structures was clearly expressed in his work. Soon followed a period where a number of reports on condensation polymerization from different starting materials appeared[15,16,17]. However, in all cases their polymeric nature was not usually understood. Thus Marcker[18] and Kraut[14] thought that pyrolysis of "salicylide" gave phenylene oxide, though undoubtedly the product was a polymer. No appreciable advance was made till about 1920 or even later from the basic understanding laid by Kraut and Lourenco. The use of a chain structure makes it necessary to indicate the nature of the end group and so some preferred ring structure. Some others who still believed polymerization as a sort of association expressed the formulae as ring structures containing two or more monomeric units the rings being held together by some sort of inter-molecular forces to give the polymer. The uncertainty which existed in the minds of the authors of this period and even later may be shown by the structural formulas (with question mark) which they assigned to the polymeric products they obtained. Thus Bischoff and von Hedenstrom[19] assigned the following formula for the product obtained by the reaction between oxalic acid and dihydric phenol



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In short, though the conception of long chain molecules and the possibility of these being mixtures of molecular species difficult to separate seems but a short step from conclusions of Lourenco and Kraut, it did take a long time for the chemist to realise this mainly because they believed every definite substance could be classified in terms of a single definite molecule capable of being represented by a concise formula. While the possibility of forming giant chemical structures composed of linear chains, branched chains, or net works was implicit in the foundations of structural chemistry, chemists generally hesitated to discard the molecule as the prime goal of their researches.

B) Vinyl Polymers

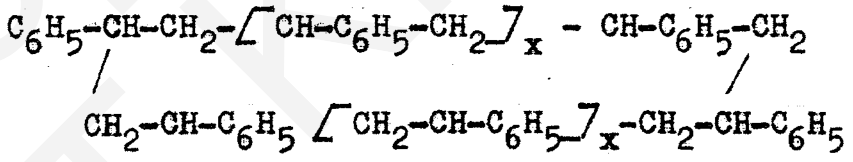
That vinyl monomers undergo polymerisation was known from almost the same time as their isolation. Thus Berthelot[20] applied the term polymerisation to the conversion of styrene to a gelatinous mass observed by Simon[21] in 1832. Polymerisation of isoprene[22] methacrylic acid[23] etc. were also reported by about 1880. But as mentioned earlier the chemists wanted to think only in terms of association of molecules as the step towards polymerisation. They gave ring structures containing four, five or even more units, which were supposed to be associated through their "partial valencies". The "colloids" thus formed were supposed to be responsible for the negligible change observed in boiling point elevations or freezing point depressions of their solutions. Though Lebedev[24,25] proposed chain structures such as $(-CH_2-CH = CH-CH_2-CH_2-CH = CH-CH_2-)_x$ for polybutadiene and recognised that polymers are of high molecular weight, he erroneously concluded that polymer is formed by a gradual passage of the monomer through successive stages of aggregation, the entire process resembling intermolecular association. In spite of the proposals of large primary valence structures for rubber by Pickles[26] and somewhat ambiguously for polybutadiene by Lebedev[24,25] prevailing opinion favoured rings of moderate size for vinyl and diene polymers. Leuchs and co-workers[27] favoured the view that strained rings (i.e. those other than five or six membered) tend inherently to polymerise by "secondary valences" of same sort.

Development of the Macromolecular Hypothesis

Staudinger[28] was the first to oppose the then existing view of formulating polymeric substances as association compounds held together by "partial valencies". He proposed chain formulas for polystyrene, polyoxymethylene, and rubber. Further the colloidal properties of these substances were attributed entirely to the sizes of their primary valency molecules. Regarding "end groups" he suggested that in such long chain structures no end groups are necessary to saturate the terminal valencies. This seemed plausible as the free radicals at the end of such long chains may remain active without colliding with active centres due to the immobility of the macromolecules. Staudinger brought forward experimental evidence against association theory. Thus he showed that rubber retains its colloidal properties even after hydrogenation[29]. Further in contrast to association colloids, high polymers exhibit colloidal properties in all solvents in which they dissolve[30]. However Staudinger's view did not find immediate acceptance. Others still preferred to believe in the finite ring formulas[31] which seemed to be supported by the erroneous results obtained in molecular weight determinations[32]. The existence of unit cells in crystalline rubber and cellulose similar in size to those of simple substances[33] revealed by x-ray diffraction studies seemed to support the view that polymeric molecules are also small. But Sponsler and Dore[34] showed that the results of x-ray diffraction by cellulose fibres are consistent with a chain formula composed of indefinitely large number of units. The cellulose molecule continues from one unit cell to the next through the crystal lattice. This interpretation made the associated ring theory untenable. Meyer and Mark also strongly advocated the long chain covalent structures. But they still continued to believe crystallites to be discrete units or micelles formed by aggregation of polymer molecules[35,36]. The length of a micelle was considered to be identical with molecular length, molecular weights of 5,000 being estimated in this manner. High values obtained for molecular weight by careful osmotic sure method were attributed to solvation. Staudinger opposed this view[37]. He believed that a polymer molecule may pass through many unit cells reaching from one end of a crystallite to the other, then meander through an amorphous region and into another crystallite, etc. Thus the covalent structure of polymers was slowly taking firm ground. In 1928, Meyer and Mark[36] proposed that the properties of vulcanised rubber are to be accounted by the formation of covalent cross-linkages. Staudinger[38] extended the covalent structure idea to differentiate between linear and non-linear polymers. The insolubility and infusibility of the latter was explained as being due to formation of net work structures.

A fairly clear picture of the polymer structure arrived at by 1929 is presented in the Annual Reports of 1929[1]. In this report polymerisation is defined as "chemical combination involving operation of primary valency forces". The picture given about natural as well as synthetic polymers is illuminating. Thus the difference between the various forms of solid polymerides of formaldehyde is accounted on the basis of difference in the end groups or due to some internal rearrangement. Again recognition was given to the fact that highly polymerised substances are not homogeneous in the sense that they are all equal in length and molecular weight and also the physical properties of the polymer depend upon its molecular weight. In polyoxymethylene series the end groups could not be detected by x-ray analysis. This was accounted for by suggesting that the linear chains are arranged parallel to one another and as these differ in length the end groups occur at irregular intervals and hence are not detectable by x-ray methods. In short the views regarding the structure of polymer in 1929 may be summarised as follows :-

The term "micelle" refers to the whole crystallite (i.e. crystalline materials formed by inter-molecular forces between unequal large macromolecules which can exist only in solid state). The colloidal properties are not due to the fact that molecules are associated in micelles as in certain soap solutions, but to the special properties possessed by long chains which are equal in size to colloidal particles. In one direction the chains are colloidal in nature while being of ordinary magnitude in the other two. The difficulty regarding the terminal valency was explained by assumption of endless chains. Thus polystyrene was given the following structure.



$$\begin{array}{l} C_6H_5-CH-CH_2-[CH-C_6H_5-CH_2]_x - CH-C_6H_5-CH_2 \\ \quad\quad / \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad / \\ \quad CH_2-CH-C_6H_5\ [CH_2-CH-C_6H_5]_x-CH_2-CH-C_6H_5 \end{array}$$

The series of brilliant investigations embarked upon by Carothers[39,40] in 1929 established the structure of polymers and the relationship between the constitution and properties of the substances. Thus by about 1930 the covalent chain concept was an almost established fact.

Soon theoretical chemists began to invade the field. Thus Kuhn[41] in 1930 published the first application of the methods of statistics to a polymer problem. He derived formulas expressing the molecular weight distribution in degraded cellulose on the assumption that splitting of inter-unit bonds occurs at random. The statistical approach has assumed an important part in the treatment of constitution, reactions and physical properties of polymeric substances which are highly complex for a direct mechanistic deduction from the detailed structures of the constituent molecules. The average size and shape and the ability of these long chain molecules to rotate about its valence bonds attracted the attention of many theoretical chemists. Their investigations provided the background for an attack on such problems as high viscosities[43] exhibited by dilute solutions of high polymers, double refraction of flow[42] and rubber elasticity[43,44].

Various properties of polymers which depend on molecular weight could not be satisfactorily elucidated till a method for accurate determination of molecular weight was evolved. Staudinger[45,46] in a number of papers published between 1930-1932 emphasised the dependance of molecular weight of linear polymers on the viscosity of their dilute solutions. Solution viscosity is a readily determinable quantity and hence relationship between viscosity and molecular weight is of great importance. Staudinger from results known at that time concluded that intrinsic viscosity is directly proportional to molecular weight.

$$[\eta] = KM$$

where $[\eta]$ = intrinsic viscosity, M = molecular weight and K = constant characteristic of the given polymer. The use of this formula gave molecular weights which were low by factors of 10 or more. Since then, molecular weights of a number of polymer series have been determined and reliable relationships between solution viscosity and molecular weight have been established. The most widely used expression is the Staudinger-Mark equation

$$[\eta] = KM^a$$

Very recently Palit[47] has put forward another expression which is claimed to fit in the values more accurately.

$$100\,[\eta]\rho_e + \ln M = K_1M^{2/3} + K_2$$

where ρ_e = partial density of the polymer in dilute solution K_1 and K_2 are constants.

CLASSIFICATION OF POLYMERS

Carothers[48] classified polymers as

i) C-polymers or condensation polymers in which the molecular formula of the structural unit lacks certain atoms present in the monomer(s) from which it is formed due to elimination of by-product, often water.

ii) A-polymers or addition polymers in which the molecular formula of the structural unit is identical with that of the monomer from which it is derived.

The importance of this classification is not in the difference in composition or of the structural unit from the monomer(s), but in the mechanism of formation of the two which are entirely different. Thus C-polymerisations proceed by stepwise inter-molecular condensation of functional groups; A-polymerisations usually follow a chain mechanism involving active centres of one sort or another. The structural units of condensation polymers usually are joined by inter-unit functional groups like ester, amide, acid anhydride etc. Most addition polymers do not possess functional groups within the polymer chain although they may be present as lateral substituents.

This type of a sharp classification is not always possible. There are border line cases. For example glycol and di-isocynate react inter-molecularly through pairs of functional groups yielding urethane inter-unit linkage without elimination of any product. But the mechanism and structure of the polymer require its inclusion in the condensation class Hence the original classification of Carothers if applied literally fails often times. It is necessary to broaden the definition of condensation polymers, to include also polymers, which on chemical degradation yield monomeric and products differing in composition from the structural units. Addition polymerisation may be defined as the process involving only scission of a bond in the monomer and reformation of similar connections with monomers (as in the opening of the carbon-

carbon double bond of an unsaturated monomer or the opening of the ring of cyclic monomer) without formation of any by-product. These two classes can again be subdivided into linear and non-linear polymers. Linear and non-linear polymers differ markedly in their structural pattern as well as in their properties.

ADDITION POLYMERISATION

Addition polymerisation has no exact parallel reaction in the classical organic chemistry. In this type an unsaturated molecule which some-how or other gets activated adds on other unsaturated molecules leading to long chain compounds and finally gets deactivated. Now it is realised that this process is a special type of chain reaction. The concept of chain reaction arose as a result of observations made on deviations from Einstein's Law of photochemical equivalence which may be stated in its original form as "If light brings about a reaction, one molecule is normally transformed for each quantum of light absorbed". Thus the quantum yield is the ratio of number of molecules reacting to the quanta absorbed must be unity. This relationship however applies only to a limited number of cases. If the quantum yield is less than one we can explain it as due to the deactivation of a fraction of the molecules before their transformation due to some collision with wall or some foreign molecule. But in many cases the value is found to be greater than one usually two, as for example photo-chemical decomposition of hydrogen iodide[49]. Einstein's Law is considered to be obeyed if the quantum yield approaches any integer upto three.

A third class of reaction exists in which the quantum yield may be in the range of 10^3 to 10^6 where Einstein' Law is not even approximately obeyed. This indicates that once the primary process namely the activation of a molecule, which requires a single quantum of light, takes place, some special type of secondary reaction which involves thousands of molecules ensues. If such a large number of molecules react due to absorption of single quantum of light it seems likely that this process must be the same for each molecule. The only simple way to explain this is to assume that the secondary process ultimately regenerates an active molecule which can continue the reaction, which may be schematically represented as follows :-

$$A + h\nu \longrightarrow A^*$$

$$A^* \longrightarrow B \longrightarrow \text{products} + A^*$$

This type of reaction is called a chain reaction, the classical example of which is the much studied photo-chemical hydrogen chlorine reaction. The three stages involved in a chain reaction are (A) chain initiation, (B) chain propagation and (C) chain termination. The process (C) can take place by collision with a foreign molecule or with the wall of the reaction vessel.

Usually the difficult step is the chain initiation process. Once it has been achieved the succeeding propagation and termination steps are often extremely fast and may take only a fraction of a second. The fact that the reaction may carry on for several hours only means that a chain reaction unlike a single stage chemical reaction proceeds by a series of "fizzles". If they were very few, the reaction would go by a series of jerks at randomly spaced intervals as can be demonstrated in the case of natural disintegration of radio active elements. The smooth overall rate observed in many chain reactions is due to the superimposition of a series of such "fizzles" all of which start at different times, thus ironing out the random fluctuations.

In any vinyl polymerisation the three elementary processes may be distinguished and Mark[50] has aptly named these phases initiation, propagation and termination. Addition polymerisation of vinyl derivatives is now accepted to proceed through a chain mechanism[51,52,53] and three stages are now discussed in detail.

A. CHAIN INITIATION

In a vinyl or diene monomer the active chain centre can be produced by heat, light or catalyst.

(a) Thermal Initiation

The chain initiation is caused by production of molecules each with a larger amount of energy than the average individual value. The proportion of molecules having an energy greater than E cals./gm.mole is proportional to $e^{-E/}$ The activation process may be written as

$$M + M \longrightarrow M^* + M$$

(b) Photo-chemical Initiation

The initiation reaction may be written as

$$M + h\nu \longrightarrow M^*$$

The activating agent is a light quantum introduced externally. In deriving an expression for the chain starting centres we have to take into account intensity of light, the fraction of light absorbed by the monomer and the fraction of absorbed quanta which is effective. Photo-chemical initiation has the following advantages :-

The rate of production of chain starting M^* molecules is independant of temperature an important point in finding out energies of activation.

It can be controlled instantaneously by external devices which alter the incident intensity immediately.

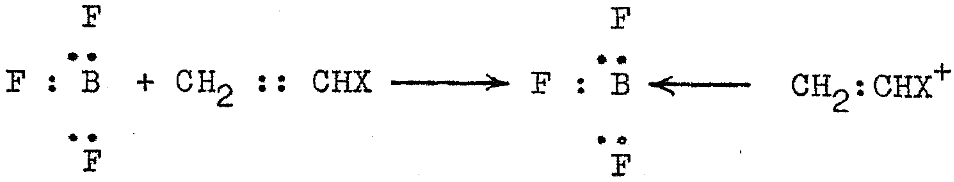
These make it possible to study the effect of temperature on propagation and termination at a constant initiation rate and to determine the life time of the active fragment. None of these advantages can be found in thermal initiation methods.

(c) Catalytic Initiation

The term "catalyst" in this connection is rather a misnomer as the catalyst is always used up during polymerization. "Catalytic initiation" is the one which is always used in large scale production of polymers because of the ease with which the rate of polymerization and the average molecular weight of the polymer formed can be controlled. The catalysts used in initiating the polymerization may be classified as (i) Ionic catalysts and (ii) Free radical forming catalysts.

(i) Ionic Catalysts

This type of catalyst includes certain inorganic salts such as boron trifluoride, aluminium chloride and stannic chloride[54] and sodium in liquid ammonia and alkali metal alkyls[5 The speed of the reaction is too high for any accurate study. Polymerizations initiated by ionic catalysts are carried out at low temperatures of the order of -80°C. The polymerization usin such type of catalysts are now believed to proceed through an ionic mechanism. Polanyi and his co-workers[56] have shown that traces of water are necessary for the cationic polymerizations to start and the accepted theory is that polarisation of the double bond of the monomer occurs, and the active ion so formed starts the chain reaction, which may be represented as below :-



$$\mathrm{F}:\overset{\mathrm{F}}{\underset{\overset{\cdot\cdot}{\mathrm{F}}}{\ddot{\mathrm{B}}}} + \mathrm{CH_2::CHX} \longrightarrow \mathrm{F}:\overset{\mathrm{F}}{\underset{\overset{\cdot\circ}{\mathrm{F}}}{\ddot{\mathrm{B}}}} \longleftarrow \mathrm{CH_2:CHX^+}$$

As the growing radical is an ion the termination reaction as well as the kinetics of the whole polymerisation is different from the polymerisation reaction initiated by free radical catalysts.

(ii) Free Radical Forming Catalysts

This type of "catalysts" decompose to give free radicals and the use of such compounds has long been recognised as a method of initiating polymerisation. Organic peroxides and azo compounds (sometimes inorganic persalts[57]) are the most widely used and effective single initiaters of this type but are surpassed in activity by systems containing both oxidising and reducing agents.

The decomposition of peroxides is formulated as follows[58] :

$$C_6H_5 - CO\text{-}O\text{-}O\text{-}CO\text{-}C_6H_5 \longrightarrow C_6H_5\cdot + C_6H_5COO\cdot + CO_2$$

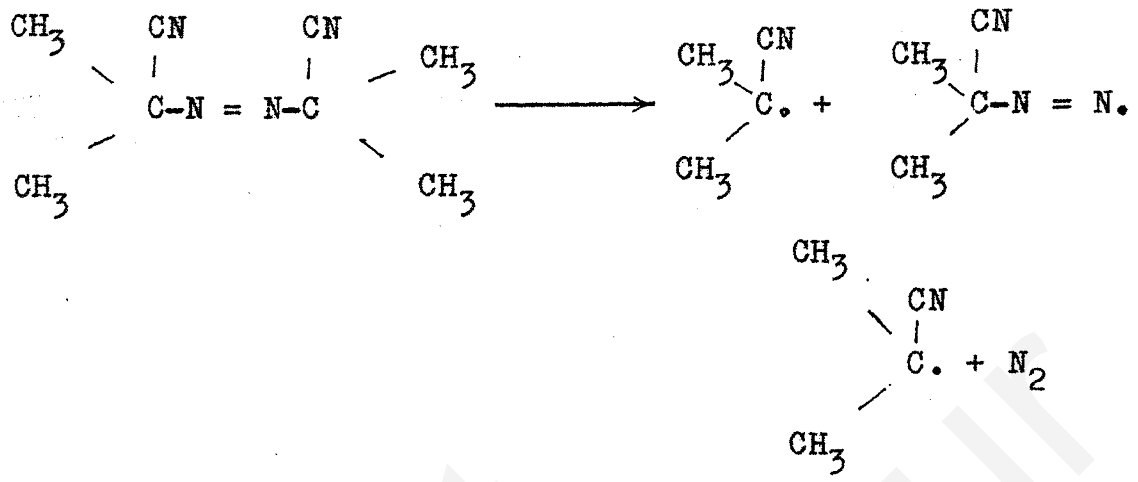
However, intensive study on decomposition of peroxides has proved that the decomposition is not so simple as represented by the above equation. Decomposition has usually a higher order than unity. Hence other reactions involving decomposition of peroxides have to be postulated[59]. This is taken to be a bimolecular induced chain decomposition. Therefore if the unimolecular decomposition reaction is to be investigated it is necessary to suppress as far as possible induced decomposition. It has been observed that many substances have the property of excluding induced decomposition in solution of which one of the most efficient is styrene[60]. Any variation in the rate of decomposition of peroxides in various solvents is due solely to the occurrence of the induced decomposition. The investigations carried out by Cooper[61] on substituted benzoyl peroxides indicate that peroxides can act as initiators as well as chain terminators. So any study using peroxide as catalyst has to take care of these side reactions.

The azo group of initiators came into prominence by about 1949 when their outstanding reactivity in promoting polymerisation of many monomers was reported[62,63]. These have the following advantages ofer the peroxide catalyst :-

(1) Though there are some minor differences in chain initiation in different monomers these differences are not so clearly marked as in benzoyl peroxide[64]. However Arnett and Petersen[65] have shown by using 2-2' azo isobutyronitrile labelled with C^{14} the efficiency of the initiator is dependant on the monomer used.

(2) Azo catalysts in general take part in no reaction other than initiation[64,66] though substances like diazo amino benzene, tetraphenyl succinodinitrile[67] etc. act both as initiators and retarders.

The decomposition of azo catalysts may be represented as shown below[68] :



The radical so formed by decomposition of either a

or peroxide catalysts then initiatesthe chain by drawing on the π electrons of the double bond of monomer and leaving the other unpaired electron to form a larger radical.

$$R\cdot + CH_2 = CHX \longrightarrow R\text{-}CH_2\text{-}CHX\cdot$$

(where R. stands for the radical formed by decomposition of the free radical catalyst). This type of a mechanism demands the presence of the catalyst fragment in the polymer chain, direct proof of which have been obtained from a number of experiments[65,69].

(d) Reduction Activation Initiation

Among the catalytic initiation is to be mentioned this fairly new method of initiation especially because of its much greater activity and its extensive applicability in emulsion polymerisation as compared with the free radical catalysts mentioned above. The discovery of this method is rather accidental and was made as a result of observation, that, not only did the induction period due to presence of oxygen decreased but the rate of polymerisation also increase much if some reducing agent is used to offset the inhibitory effect of oxygen. Research in this line by a number of workers[70] resulted in the discovery of what is now known as reduction-activation (Redox). Examples of this type are (1) hydrogen peroxide ferrous salts (2) organic peroxides with reducing agents such as phenyl sulfinic acid, formic acid, phenylhydrazine thio- β -naphthol and polyamines etc.

(e) γ-radiation as a Method of Initiation

It may be mentioned that the use of γ -radiation in initiating polymerisation[71] is now becoming popular and has been studied by a number of workers. This radiation give rise to both ions and free radicals in liquids.

B. CHAIN PROPAGATION

The propagation mechanism depends upon the fragment which initiates the chain. If the initiation is caused by ionic catalyst the growth occurs through a process which retains this ionic character which may be represented as shown below :

$$RM^+ + M \longrightarrow RM_2^+$$

$$RM_n^+ + M \longrightarrow RM_{n+1}^+$$

In thermal and photo initiated gas phase polymerization the problem of whether the growing macromolecule is a free radical or an energetically excited molecule is still open to question. However it is quite probable in gaseous photopolymerizations both types of carriers exist. In fact the experimental results seem to indicate in the case of methyl methacrylate[72] chloroprene[73] and vinyl acetate[74] two types of reactions can be induced to occur.

In liquid phase polymerization a free radical intermediate is now favoured almost exclusively. The fact that nonionic chain initiators produce radicals and many polymerization inhibitors themselves are known to destroy free radicals support this idea. The chain propagation step consists essentially of a free radical attack at one of the doubly bonded carbon atoms of the monomer. One electron of the double bond pairs with the odd electron of the free radical to form a bond between the free radical and this carbon atom, the remaining electron of the double bond shifts to the other carbon atoms which becomes a free radical. In this way the active centre shifts uniquely to the newly added monomer which is thereby rendered capable of adding another monomer etc

$$R^{\bullet} + CH_2 :: CHX \longrightarrow R^{\bullet\bullet}CH_2 : CHX^{\bullet}$$

$$R\text{-}CH_2\text{-}CHX^{\bullet} + CH_2 :: CHX \longrightarrow R\text{-}CH_2\text{-}CHX : CH_2{:}CHX^{\bullet}\ e$$

What ever be the exact nature of the active fragment the basic propagation process may be written as

$$RM_1 + M \xrightarrow{K_p} RM_2 \quad \ldots \quad A$$

$$RM_2 + M \xrightarrow{K_p} RM_3 \quad \ldots \quad B$$

$$RM_n + M \xrightarrow{K_p} RM_{n+1} \ldots \quad C$$

The same reaction constant is written for each propagation step irrespective of the chain length of the growing radical. This principle of equal reactivity of functional groups has been proved experimentally.

Rate of reaction studies on a series of homologous series like esterification of mono basic and dibasic acids[75], saponification[76] and etherification[77] show that significant change in the velocity constant with chain length is confined to the lowest members of the series, but the velocity constant rapidly approaches an asymptotic value as we go higher up the series.

Kinetic studies on the degradation of various polymers by reactions which bring about scission also support this view. Thus for example alcholysis of polymeric decamethylene adipate[78] by limited amounts of a higher alcohol or glycol show that over the range studied the mean reactivity of inter unit bonds shows no change.

Again when in a polymer chain the lateral substituents undergo reaction without altering the degree of polymerisation as in the saponification of polyvinyl acetate[79] the velocity of reaction (in this case velocity of saponification) is very nearly the same as that for the lowest member of the series (in this case ethyl acetate) under the same conditions.

Theoretical considerations also support this view that the reactivity of every like functional group is the same irrespective of the size of the molecule to which it is attached. Arguments put forward in favour of a decrease in reactivity of functional groups with the size of the molecules to which they are attached have arisen from considerations of mechanics of interaction of these functional groups rather than from any inherent abnormal character of the functional group themselves. It is true that large molecules diffuse slowly. But this does not mean that collision rate of functional group also decrease correspondingly. The mobility of the functional group is much greater than indicated by the macroscopic viscosity of the molecule as a whole. Though the range of diffusion of the terminal functional group within an interval of time, which is short as compared with the time required for the displacement of the molecule as a whole, will be limited, it can diffuse over a considerable region through rearrangements in the configuration of the nearby segments of the chain. Hence its frequency of collisions with the immediate neighbours occur at a rate which is atleast not much less than that occurring in simple liquids. In other words the actual collision frequency has little relationship to the mobility of the molecule as a whole. As Rabinowitch and Wood^{80} have shown a pair of neighbouring molecules or functional groups collide repeatedly before diffusing apart. Hence when the rate of diffusion is slow the series of encounters between the groups are prolonged. Thus decreased mobility affects the time distribution of collisions experienced by a given functional group. But the collision rate averaged over a time, which is long as compared with the time required for diffusion from one partner to the next, will not be affected to any great extent. Even if the collision frequency is reduced somewhat by the decrease mobility as polymerisation progresses, the duration of the collided state increases. Hence the concentration of pairs of functional groups sufficiently close together to permit reaction between them to occur is independent of mobility.

In addition polymerisation as mentioned earlier the propagation reaction occurs by addition of monomer to the growing chain. The mobility of the monomer will be comparatively little affected by increasing viscosity of the medium. Hence it can maintain an equilibrium concentration in the vicinity of the active centres. Therefore, even though the chain growth process in vinyl polymerisations is relatively rapid (one in 10^9 collisions) diffusion would not be expected to be rate controlling. However the chain termination step involving collision between two growing radicals which occurs much more frequently (one in about 10^5 collisions) it is not improbable that diffusion, particularly when the viscosity of the medium is high, may become rate controlling.

Another strong argument advanced in favour of a decreased activity of functional groups attached to big chains, is that the latter may shield the functional group from reacting with other molecules. This also does not seem to be a very valid argument. Except in very dilute solutions where the irregularly coiled molecules can exist more or less independently of one another, the polymer chains intertwine extensively in a most irregular fashion with the result that the functional group which shows no preference to units of its own chain will in general be surrounded by units belonging to various other molecules. Thus the chains act like so much diluent and are appropriately taken into account by writing the rate expression in terms of concentration of functional groups participating in the reaction per unit volume and not in terms of molefractions of molecules.

The above discussion makes it clear that there is no valid justification in assigning a generally abnormal chemical reactivity to polymer systems and we are perfectly justified in assuming the propagation reaction rate constant, remains constant irrespective of the size of the molecule with which reaction takes place. The application of these principles presupposes a homogeneous reaction. Exceptions to these generalisations may be found only

(1) where the specific rate constant is very high while at the same time owing to the size of the molecule and/o to viscosity of the medium the diffusion rate is low in which case diffusion may become rate-determining and the process wil proceed more slowly than standard kinetic extrapolations would predict, and (2) when the solution is very dilute that each growing macromolecule is capable of independent existance in which case shielding of the functional group is possible thus reducing the rate of reaction.

Exception to the principle of equal reactivity of everylike functional groups may also occur among the very lowest species in the polymer mixtures. This principle makes the application, of statistical considerations to the problem of distribution of bonds formed during polymerisation, possibl which help one to arrive at the constitution of polymers. Further it immensely simplifies the kinetic treatment of polymerisation reactions for it permits total disregard of the complex array of molecules participating in polymerisation thus enabling us to put the same constant for the propagation steps as represented in equations A, B and C on page 25.

Irrespective of the particular chain propagation mechanism ionic, free radical or energetically excited molecule, the entire synthesis of an individual polymer from monomers occurs with in a brief interval of time whereas the overall conversion of monomer to good yields of polymer may require hours which is the characteristic of any chain reaction. Thus in addition polymerisation at any stage of the process we find only high polymer and unchanged monomer and not polymers of intermediate stages of growth. Also the average molecular weight remains approximately constant with extent of conversion to polymer. But in condensation polymerisation, which proceeds through independent condensations occurring at intervals scattered over the period during which polymerisation is carried out and not during a single comparatively brief interval as in the case of addition polymerisation, interruption of the reaction at the early stages yield polymers of low molecular weights and the amount of monomer in system will be negligible (less than 1%). In vinyl addition polymerisation high polymer makes its appearance at the outset. In contrast to condensation polymerisation they proceed quite rapidly and polymers of molecular weights of the order of 10^5 to 10^7 are readily obtainable.

C. THE TERMINATION REACTION

The mechanism of termination depend on the nature of the growing polymer. Any mechanism proposed has to account for the loss of activity of a growing chain. The various methods by which a growing chain may get deactivated come under any of those discussed below :

(a) <u>Spontaneous Termination</u>

The growing chains "die" spontaneously in the bulk phase or get deactivated by collision with the walls of the reaction vessel. If the growth occurs through an activated double bond mechanism, this is quite plausible, and for such a type of growth spontaneous termination merely implies deactivation to a "dead molecule" with the same structure. When the growing chain is of the free radical type some sort of internal rearrangement (usually a hydrogen atom transfer along the chain) has to take place to give a molecule with all its valency satisfied. In ionic polymerisation spontaneous termination can take place by splitting off a proton from the growing macromolecular ion which results in leaving behind an unchanged polymer incapable of further growth. The proton produced may initiate another ionic chain and continue the polymerisation. Such a process by which a growing chain gets terminated by expulsion of an ion (or atom in the case of free radical chains) from some molecule in the system, at the same time liberating an ion (or radical) capable of initiating a chain, is called a "transfer reaction". Thus a transfer reaction is not a true termination because a number of such reactions can go at the same rate as a single chain growth and use up the same total number of molecules so that the overall rate remains unaffected and some other mechanism must be there to destroy the active chain. Transfer reaction can however be detected by molecular weight studies, because the total number of chains formed will be greater than the number of initial active centres.

The idea of transfer in non-ionic polymerisations was first introduced by Flory[81] to explain various features in pure monomer polymerisations.

In solution polymerisations more direct evidence of transfer can be obtained, for example styrene polymerised in a number of solvents with the same overall velocity, but yielding polymers of different molecular weights[82]. The changes in molecular weight can be explained only on the assumption of transfer reaction, if we assume that propagation and termination steps are unaffected by solvents so that initiation rate remains the same. More direct proof of transfer in solvents was obtained by chemical analysis of polymers for the presence of solvent fragment. Thus poly-styrene obtained by polymerisation of styrene in solution in carbon tetrachloride was found to contain chlorine atoms[83]. This is possible only if chain transfer reaction occurs with solvent molecules, for if $RM_n\cdot$ is the growing free radical and transfer takes place with CCl_4 the reaction may be represented as

$$RM_n\cdot + CCl_4 \longrightarrow RM_nCl + CCl_3\cdot$$

The $CCl_3\cdot$ radical generated as a result of transfer can start off another chain which again will contain chlorine atoms. The experiments also prove the nature of the growing chain to be of a free radical type because phenyl radicals produced in presence of carbon tetrachloride are known to give chlorobenezene and hexachloroethane amongst other products[84].

$$C_6H_5\cdot + CCl_4 \longrightarrow C_6H_5Cl + CCl_3\cdot$$

$$2\ CCl_3\cdot \longrightarrow C_2Cl_6$$

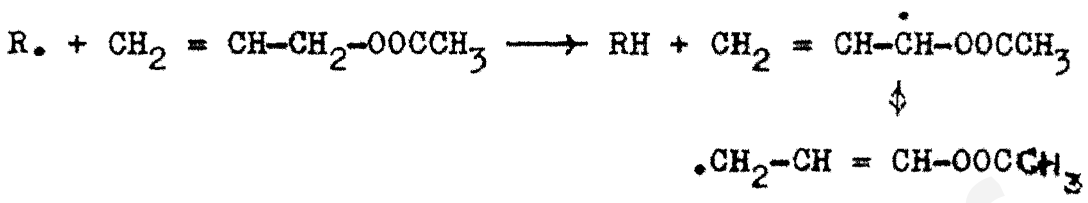
From these observations we can conclude that transfer may occur in all solution polymerisations and in pure liquid phase also.

(b) Monomer Termination

In polymerisation reaction the chain grows by addition of monomer. This addition is the result of number of collisions. As the process of reaction has an activation energy only a small fraction of collisions will cause the reaction to take place. Further the collision must be with the reactive end of the growing chain. Hence only those collisions which take place in a specified way with the energy requirements also satisfied, will result in reaction. Melville[85] has estimated that only one in 10^6 collisions are successful. Therefore a number of collisions are "neutral", that is, they neither add on nor deactivate the growing chain. But it is possible that some collisions, which will definitely be few in number and much less than the fraction of successful collisions which effect addition of monomer, may deactivate the chain to a "dead" species. Such a process is termed monomer termination. The photochemical polymerisation of acetylene[86] is thought to be terminated by such a type of reaction.

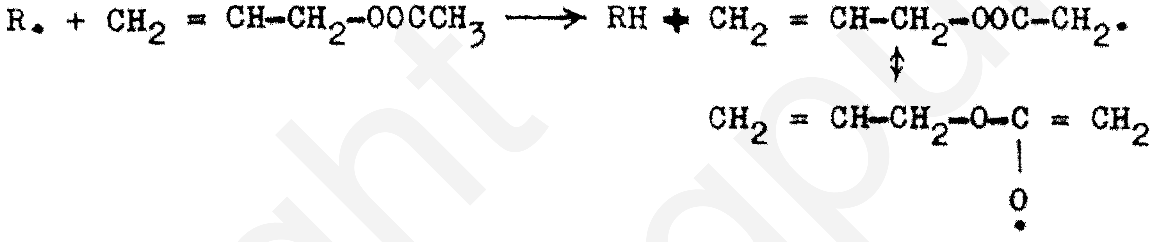
The termination mechanisms discussed so far involve one growing chain. Therefore the overall rate of reaction will be directly dependent upon the rate of initiations. But the destruction of free radicals almost always happens as a result of mutual interaction of two radicals which mechanism, if operative, demands that the overall rate of polymerisation must be proportional to the square root of the initiator concentration. But some polymerisation reactions which are definitely known to proceed through a free radical mechanism are found to show a linear relationship with rate of initiation. Examples of this type are allyl compounds[87,88] and vinyl benzoate[89]. Polymerisation of the allyl compounds lead to polymers of low degree of polymerisation. The above features of this class of compounds may be explained in the following lines[87] :-

A free radical can be removed only by interaction with another free radical. Hence if termination process involves only one free radical, it means, that the radical produced by the action of the growing chain with the terminating molecule (monomer termination) must be incapable of initiating further chains. This will be true if the new radical is sufficiently resonance stabilised. Such a reaction has been termed as degradative chain transfer by Bartlett and in the case of allyl acetate it can be formulated as



$$R\cdot + CH_2 = CH-CH_2-OOCCH_3 \longrightarrow RH + CH_2 = CH-\dot{C}H-OOCCH_3 \;\updownarrow\; \cdot CH_2-CH = CH-OOCCH_3$$

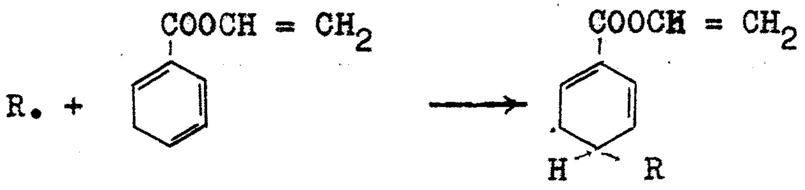
or,



$$R\cdot + CH_2 = CH-CH_2-OOCCH_3 \longrightarrow RH + CH_2 = CH-CH_2-OOC-CH_2\cdot \;\updownarrow\; CH_2 = CH-CH_2-O-\underset{\underset{O\cdot}{|}}{C} = CH_2$$

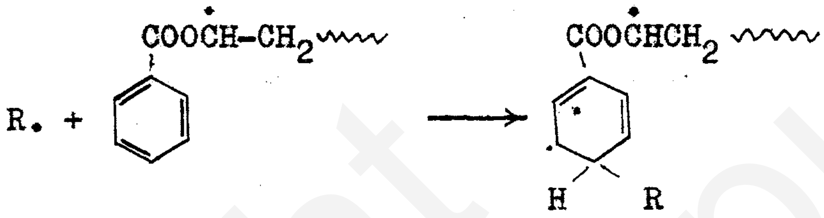
The first of these reactions is preferred because vinyl ace is found to polymerize to give long chains. Gaylord and Ei have concluded from their study on a number of allyl esters that both of the reactions occur in different allyl esters. The resonance energy of the allyl radical has been estimate to be about 25 K Cal./per mole which is sufficient to accou for the low reactivity[90].

In the case of vinyl benzoate,, cross linking h been observed above about 80% conversion to polymer[91]. Thi has been explained as due to a transfer reaction between gr ing radicals and dead polymer molecules or to the aromatic nucleus of the monomer. The reaction gives rise to a stabilised radical R'



(R')

or,



(R')

This radical is sufficiently inert to react only slowly with the monomer to carry on polymerisation chain. Consequently rate of polymerisation of vinyl benzoate is much less than vinyl acetate. It is plausible that this type of transfer reaction would lead to over linking if termination occurs by coupling of radicals. This reaction thus resembles degradative chain transfer and we can expect the rate of polymerisation to be linearly dependent upon initiator concentration as was observed by Burnett and Wright[89].

There is yet another class in which both first order and second order termination with respect to the propagating radicals appear to be operative. For example it has been found that in the photo-polymerisation of vinyl chloride, the intensity exponent for the reaction is greater than 0.5. This was explained on the basis of another type of degradative chain transfer in which chlorine atom from the monomer is abstracted by the growing chain leaving a vinyl radical which appears to be incapable of initiating polymerisation[92,93].

(c) Mutual Termination

Kinetic studies in many cases of polymerisation indicate that two growing chains take part in termination. A termination reaction of this type can take place in two ways.

(i) Combination or Coupling

When two growing chains combine with each other to give a "dead" polymer the process is termed combination or coupling. The chains growing either through an activated double bond or radical mechanism may terminate by this process as follows :-

$$\sim\!\sim CH = CHX^{*} + CHX = CH \sim\!\sim^{*} \longrightarrow \sim\!\sim CH_2{-}CX = CX{-}CH_2 \sim\!\sim$$

$$\sim\!\sim CH_2{-}CHX\cdot + \cdot CHX{-}CH_2 \sim\!\sim \longrightarrow \sim\!\sim CH_2{-}CHX{-}CHX{-}CH_2 \sim\!\sim$$

However it is not possible to say whether this combination occurs in a head to tail or head to head fashion. Further only a small proportion of the collisions with the growing chains will be effective in terminating the chains as with monomer termination. If the growing chain is ionic in character this type of a mechanism is not applicable since deactivation of such a chain can be achieved only by splitting of a cation (or anion if the propagating chain is initiated by anionic catalysts) or by combining with the oppositely charged ion.

(ii) Disproportionation

In this type transfer of an atom takes place between the two chains to give a saturated and an unsaturat molecule

$$\sim CH_2-CHX\cdot + \cdot CHX-CH_2\sim \longrightarrow \sim CH = CHX + CH_2X-CH_2\sim$$

Analogous reactions are encountered in a number of free rad cals as for example ethyl and phenyl ethyl radicals disproportionate as shown below.

$$2\ C_2H_5\cdot \longrightarrow C_2H_4 + C_2H_6$$

$$2\ C_6H_5-CH_2-CH_2\cdot \longrightarrow C_6H_5-CH = CH_2 + C_6H_5-CH_2-CH_3$$

As combination and disproportionation give the same rate equation it is not possible to decide which bring about termination by kinetic study alone. However molecula weight measurements will be decisive as, if termination occ by combination only, the total number of chains will be hal the number of chains started, whereas, if it is by dispropo tionation only, the two quantities should be the same.

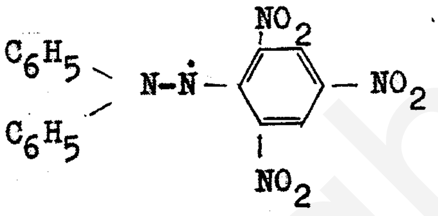
The precise nature of the termination step is a very difficult problem. Evidence for both sides is strong. Evidence of the exact nature of termination is derived from two sources namely direct study of polymerisation reactions and the products obtained from reactions which are known to involve small radicals. But the results of investigations of transfer constant of styrene in carbon tetrachloride[94] indicate that the size of radicals has effect on their reactivity. Hence the safest course of studying the termination reaction is to investigate separately each polymer reaction than to draw conclusions from the behaviour of structurally similar small radicals. In the case of photo-polymerisation of liquid vinyl acetate, Burnett and Melville[95] from osmotic molecular weight measurements conclude that termination is by disproportionation while in redox polymerisation of methyl methacrylate Baxendale etal[96] think that termination is by combination. In these cases transfer reaction is supposed to be absent. Hence this end group determinations are not very informative. Size distribution for the two mechanisms will be different and hence its study will be informative in deciding between the two.

In this mutual termination mechanism we discussed only about termination involving two growing radicals. But we cannot overlook the possibility of termination of the growing chain by collision with free radical from catalyst the importance of which was stressed by Palit etal[97] in 1949. They have discussed the extreme case of termination occurring entirely by reaction with free radical from catalyst and have shown that the overall rate of polymerisation will be proportional to the square of the monomer concentration and also that size distribution decreases exponentially with no maximum. Therefore the effect of radical termination occurring concurrently with termination by combination will be that the overall rate of polymerization will be proportional to a power (lying between one and two) of monomer concentration and a shift in the maxima of size distribution curve towards lower chain length.

INHIBITORS AND RETARDERS

Like all chain reactions, polymerizations are also very sensitive to traces of foreign molecules and this has important technical applications. Thus the thermal, uncatalysed styrene and methyl methacrylate polymerizations[98] are very sensitive to traces of oxygen. If the "foreign molecule" reacts with chain radicals to yield either non-radical products or radicals of such low reactivity as to be incapable of adding monomer, the normal growth of polymer chains will be suppressed. Such a substance is termed "inhibitor" if it is so effective as to reduce the rate of polymerization to zero. But if its action is less effective and is able only to reduce the rate and degree of polymerization and not to suppress polymerization completely it is termed a "retarder". Thus the difference between inhibition and retardation is one of degree rather than any fundamental property of the system.

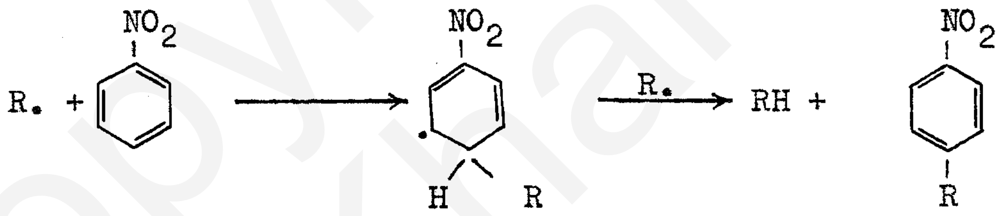
If the inhibitor itself is a free radical the product of reaction with a chain radical will have no unpaired electron, which will be incapable of adding more monomer. But the free radical inhibitor must be of sufficiently low reactivity that it will not also be able to start off a chain. The stable free radical 2,2 diphenyl-1-picryl-hydrazyl



is an extremely effective inhibitor, which gives no evidence of initiation[99]. Each hydrazyl radical consumed stops one chain radical[99,100]. This property of a "true inhibitor" as called by Foord[101] can be made use of indetermining the rate of chain initiation. If the inhibitor is not so strong all active centres will not be destroyed and polymerisation takes place with no or very small induction period, but at a slower rate than normal.

In some cases non-chemical inhibitors are also known to exist. Thus it has been observed that inert gases slow down the photo polymerisation of gaseous vinyl acetate[102]. This result suggest that in solution polymerisation the solvent itself may act as a weak inhibitor as well as a transfer agent.

The second main type of inhibitor (retarder) acts by providing an easy alternative to the normal process of chain growth and termination. As has already been stated the reaction between a free radical and a molecule always gives rise to a new radical. Therefore if molecular retardation has to stop chain growth the radical formed by its action with the chain radical must be incapable of intiating further chains. This will be the case if the radical generated is stabilised in some way. This has been postulated by Price[103] to explain the behaviour of nitro compounds as retarders. The new radical is assumed to be incapable of reacting with monomer (or does so only slowly, but it may react with another growing chain. The mechanism is as follows :



An interesting feature of this class of compounds is that their ability to effect retardation is not universal (e.g. p-benzoquinone[104,105]). In short the exact mechanism of inhibition and retardation is still not always clear. However, this class of compounds is used extensively in industry as stabilisers for monomers and for controlling the rate of polymerisation and molecular weight and size distribution of the polymers formed.

BRANCHING AND CROSSLINKING

Branching and crosslinking were often suggested to explain the discrepancies in osmotic and viscosity molecular weights of various polymers. Of the first proposed mechanisms, the one given more emphasis was that the branch starts from a monomer which has linked itself sideways. The presence of methyl group in poly ethylene[106] seemed to support this view. A more promising mechanism viz. abstraction of hydrogen from a tertiary carbon atom by a growing radical was suggested from the observations that vinyl polymers can be vulcanised by benzoyl peroxide[107] and a free radical can abstract hydrogen atom from a tertiary carbon atom[108]. Branching can also occur by chain transfer with monomer. Though in polymers obtained from monomers with the chain transfer constants less than 10^{-4} (e.g. styrene[109]) non-linearity may not be appreciable, it is by no means negligible for those obtained from monomers like vinyl acetate[110,112] whose transfer constants are comparatively high. Polymerisation and copolymerisation of divinyl compounds can also lead to non-linear products.

COPOLYMERISATION

The above discussions were more or less limited to polymerisation of a single vinyl compound. But many industrially important reactions are carried out using mixtures of monomers each capable of independent polymerisation. In some cases "monomers" which do not polymerise by themselves (e.g. maleic anhydride) are found to undergo copolymerisation. Extreme cases in which neither of the original monomers are capable of polymerising alone, but do interpolymerise are also known[111].

Although copolymerisation reaction appears to have been recorded as early as 1914 by Klatte[112]. Only recently thorough investigation of this type of reaction was made, the impetus being given by the modifications possible in the properties of the unit polymers. It is always necessary to find out whether the product obtained by polymerisation of a mixture of monomers is only a mixture of polymers of the different monomers or one in which the various monomers are interlinked. This can be easily understood by fractionation of the product, and analysis of each fraction for the copolymer composition.

Copolymers possess properties which are not shared by physical mixtures of the polymers of the components. They often retain the good qualities of their components, while physical mixtures only succeed in emphasising the bad ones. In general, if two vinyl polymers have very different physical and chemical properties a polymeric material with intermediate properties depending on copolymer composition will be formed upon copolymerisation. When the ratio of one monomer to the other is controlled the properties of the monomer present in greater proportions will predominate.

From both theoretical and practical stand points, copolymerisation constitutes a very important branch of the study of the polymerisation process. If restricted to single monomer polymerisation, the number of possibilities are limited, but by copolymerisation a great number of materials are possible. The maximum application of copolymer till now is in making synthetic rubber, as, homopolymers of isobutylene, butadiene etc. have many technical disadvantages which could be improved by copolymerising them with suitable monomers. Fresh types of copolymers are being continually studied as this is the most convenient method of getting a polymer with desired physical properties.

SUBSTANCES CAPABLE OF UNDERGOING VINYL TYPE OF POLYMERISATION

It is well known that vinyl type of compounds contain one or more unsaturated carbon linkages. The heat of reaction, for the reaction between double bonds is considerable, and consequently the molecules must become sufficiently energised before a reaction can take place. The resultant molecules remain energised and are ready for further reaction unless the excess energy is somehow removed. Taking the simple case of ethylene according to Lewis theory four out of the twelve outer electrons go to form a double bond. The classical theory does not differentiate between the two bonds. The application of quantum mechanics however reveals the difference between first order valency electrons (or σ electrons) and the second order valency electrons (or π electrons). The former possesses axial symmetry while the latter do not. It is these π electrons in which we are interested in the study of polymerization. In the lowest energy state the π electrons occupy the same bonding orbital and possess antiparallel spins. When one of the two π electrons is promoted to a non-binding state by activation, two states are possible namely the singlet state in which the spins are paired and a triplet state in which the spins are not paired. From consideration of oxygen molecule as well as spectroscopic evidence, the conclusion to be drawn is that the triplet state is not far removed from the ground state. Thus the passage from ground state to singlet state requires ~ 42 K.cal./mole and a normal frequency factor of $\sim 10^{11}$ and to triplet state activation energy is only 23 K.cal./mole and a low frequency factor $\sim 10^{4}$. Hence polymerization takes place by activation to the triplet state. The effect of substitution and conjugation normally affects the energy transition from ground to triplet state. Conjugation lowers the value, so does electro-negative substituents like phenyl, halogen, carboxyl etc. However polymerizability does not depend solely on this as may be clear from the fact that vinyl fluoride[113] does not polymerise, vinyl chloride[114] and bromide[115] polymerise quite smoothly while vinyl iodide[116] is less reactive.

In general ethylene and substituted ethylenes of the type $CH_2 :: CHX$, $CH_2 :: CX_2$ do undergo polymerization. Tetra substituted ethylenes with the exception of tetra Fluoro ethylene usually do not polymerise, though some of them undergo copolymerisation readily with other monomers.

MEDIUM OF POLYMERISATION

Our discussions in the previous pages were limited mainly to polymerisations in homogeneous media namely in bulk or in solution. The investigations reported in this thesis are directly concerned only with this type of polymerisation. However two other modes of polymerisations are also in common practice :

(i) Polymerisation in suspension

It is also known as pearle or bead polymerisation. In this case a mixture of the monomer, water and a suspension stabiliser is shaken at the required temperature with a catalyst such as benzoyl peroxide. The polymers can be isolated from the suspensions in bead like particles. A review of such type of polymerisation process has been made by Hohenstein and Mark[117].

(ii) Polymerisation in emulsion

A simple emulsion system contains monomer, water, an emulsifying agent and a catalyst. Catalysed emulsion polymerisations appear to have been disclosed first in the publications of Dinsmore[118] and Luther and Heuck[119]. Their patents disclose the simultaneous use of water and monomer soluble catalysts and soap or related substances such as sodium or potassium oleate and sodium butyl naphthalene sulphonates. The advantages of this process is efficient heat dissipation, and production of higher molecular weight products than in bulk or solution polymerisation. A general theory on the mechanism of polymerisation in emulsion has been suggested by Harkins[120] in 1947.

The above processes are not considered in any further detail as we are not directly concerned with these heterogeneous polymerisation media in our investigations reported in this thesis.

REVIEW OF THE WORK DONE ON VINYL ESTERS

Of the vinyl esters, vinyl acetate has been studied extensively. The earlier reports on the investigations of vinyl acetate are rather contradictory, due to want of adequate purity of monomer, particularly due to presence of acetaldehyde as impurity. Thus at first it was reported that vinyl acetate undergoes thermal polymerisation though Cuthbertson[121] demonstrated that it does not undergo polymerisation at 100°C in absence of initiators. Chain transfer constants for vinyl acetate in a number of solvents have been determined recently by Palit etal[122]. Of the vinyl esters of aromatic acids vinyl benzoate has also been studied by different workers[89,91].

Systematic study on the effect of reaction conditions on the polymerisation and on the properties of the polymers obtained from vinyl esters of long chain fatty acids may be said to have been initiated by D.Swern etal. However reports on the polymerisation of vinyl esters of higher fatty acids began to appear from 1933 onwards. But the results reported by earlier workers seem to be contradictory. Fikentscher[123] reported that vinyl esters of oleic, stearic and coconut oil fatty acids do not polymerise whereas Reppe[124-126] stated that vinyl esters of long chain acids can be polymerised by the normal methods. Beyond brief qualitative characterisation of those polymeric vinyl esters the early literature contains no information on their kinetics of polymerization, mechanism of reaction or their properties.

The preparation of most of these esters are reported only in patents and usually with little or no experimental detail. Furthermore, no mention regarding the purity of starting materials or final products was made. It is highly probable that the impurities present in the system were responsible for the contradictory results obtained by the earlier workers. In 1948, D.Swern etal[127] embarked upon a study on the preparation and characterisation of vinyl esters of a number of aliphatic acids by acidolysis of vinyl acetate according to the procedure of Toussaint and MacDowel[128]. The esters can also be prepared by the action of acetylene on the corresponding fatty acids in presence of catalysts like mercuric salts[124,125].

Studies on the polymerisation and copolymerisation of the vinyl esters of long chain aliphatic acids reported so far were mainly concerned with some physical properties of the plastics obtained. Thus the copolymerisation of vinyl oleate and vinyl acetate reported by D.Swern[132] was carried out with the main object of changing some of the mechanical properties and physical characteristics of the copolymer by varying the copolymer composition. Preparation, polymerisation and copolymerisation of a series of vinyl esters of long chain fatty acids starting from caproic acid to stearic acid were conducted by D.Swern etal[127]. The study mainly centered around investigations of the solubility of these polymers in various solvents and their physical appearance. W.S.Port etal[133] reported polymerisation of vinyl caprylate, caprate, laurate and myristate in bulk, dispersion, solution and in emulsion. Methods of isolating and purifying the polymers are also described. They have made some measurements of molecular weight of the polymers by osmotic pressure and light scattering methods and detĕrmined their first order transition points. They found that in bulk polymerisation using 0.25 to 0.5 mole percent of benzoyl peroxide, the induction period decreased and the rate of polymerisation increased as the temperature at which the reaction was conducted, was raised. Homopolymerisation of these esters in solution have been reported by them as producing unbranched and completely soluble polymers. In 1953 the same authors[134] investigated the copolymerisation of vinyl acetate with vinyl palmitate, stearate & oleate.They prepared copolymers having a very wide range of composition, determined the monomer reactivity ratios and the first order transition points; and where no first order transition points could be obtained, brittle point measurements were made. The use of polyvinyl esters (palmitate and stearate) and copolymers with vinyl acetate as viscosity index improvers have been studied by W.S.Port and coworkers[135]. In 1953 a report on the copolymerisation of vinyl stearate with vinyl chloride[136] and the possible uses of this type of copolymer with widely varying properties depending upon the copolymer composition, has appeared. In 1955 a study on the copolymerisation of vinyl caproate with vinyl chloride was made by D.Swern[137].

This brief review of the work on polymerisation and copolymerisation of vinyl esters of long chain fatty acids reveals the technical importance of the plastic that can be prepared from them. But it may be noted that a thorough study of the reaction mechanism and the behaviour of the polymer in solution has not been made till now. A knowledge of these is of considerable importance in developing any technically important polymers.

SCOPE OF THE PRESENT WORK

The present age is an age of synthetic materials. Synthetic polymers are replacing and supplanting natural products due to their availability, cost and adaptability. Physical and mechanical properties of polymers depend on their chemical structure and composition. It is well known that relationship exists between structure and properties. But it is still not possible to predict quantitatively properties from structure. Special properties of polymers are attributable to the size and shape of molecules. Branching and crosslinking generally complicate the linear structure. A vinyl polymer with a given chemical composition, may have several different structures. The average molecular weight, orientation of the monomers, the degree of branching, the sequence of lengths of the monomers in a copolymer, may all vary and have significant bearing on the mechanical properties. The conditions of polymerisation, as catalyst, temperature, presence of chain transfer agents among others have a marked effect on the average molecular weight, orientation, branching etc. when polymers are synthesised, not all the molecules grow to the same size. Considerable spread in the sizes and molecular weights of the individual molecules exist. Molecular weights are measured by measuring the colligative properties as osmotic pressure, freezing point depression etc. which are determined only by the total number of molecules. Constitutive properties such as viscosity, scattering of light, rate of diffusion etc. are determined not only by the number of molecules, but also by their shape, size, flexibility etc. Interest in the study of colligative and constitutive properties of macromolecules continues with unabated interest, along with kinetic studies and the studies on mechanism of polymerisation process.

In the present stage of development of High Polymer industries and science, perhaps practically every conceivable type of polymers have been prepared in the laboratories and industries, though only few are prepared on a large scale. Advances in recent years have been made in the discovery of new and more efficient initiators rather than in the discovery of any new polymers. However, in the field of synthesis and investigations on modifications of high polymers to give better products, by copolymerisation or by incorporation of newer types of plasticisers, enormous scope exists at the present time.

Syntheses of monomer from readily available raw materials, study of kinetics of their polymerisation, investigation of the properties of the macromolecules in solution are some of the problems that have interested us in the laboratory. Investigations on vinyl esters of aliphatic and aromatic acids seemed to be a fruitful field of studies. Certain peculiarities in the polymerisation of vinyl esters have been observed in that the molecular weight of the polymers increase with conversion[140] which is generally centrary to expectations from vinyl type of polymerisation. Kinetic investigations of polymerisation of vinyl esters, apart from studies on vinyl acetate, have been meagre[139] and it seemed worthwhile to pursue the studies in more detailed manner. Polymerisation characteristics of vinyl-normal esters and vinyl iso-esters of aliphatic acids and the properties of these macromolecules in solution were considered to show certain distinctive features. Investigations on the kinetics of polymerisation of vinyl n-butyrate and iso-butyrate, vinyl n-caproate and vinyl iso-caproate and the study of the characteristics of these macromolecules in solution was undertaken as a first step in the program of work in the laboratory and forms major subject matter of the thesis. In addition, solution polymerisation and copolymerisation reactions of some of the esters have been studied and forms part of the thesis.