INTRODUCTION

CHAPTER I

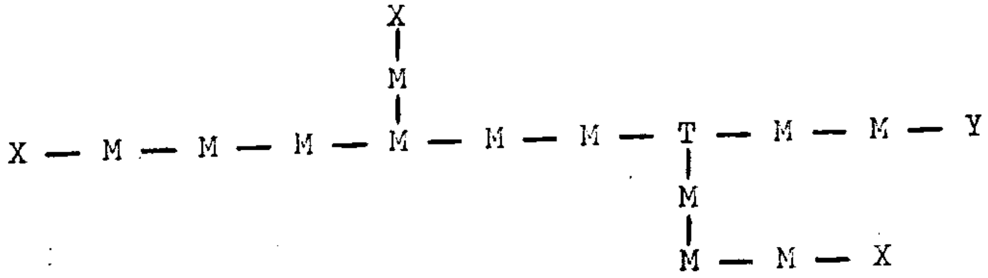
INTRODUCTION

1. General Characterization :

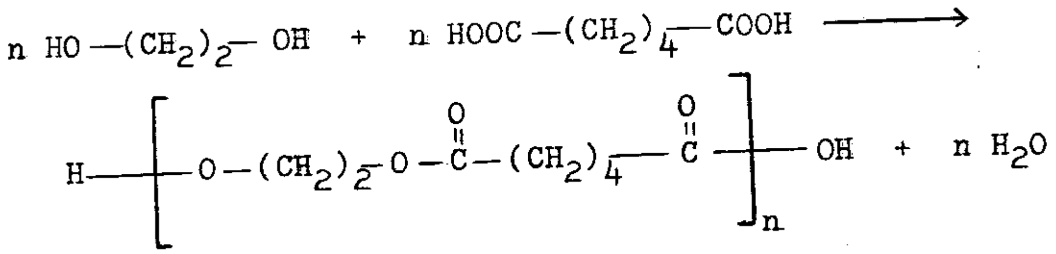
The word polymer was first used to describe compounds with the same composition but different molecular weights. The structure of polymer is generally described in terms of its structural unit(1). Structural units are groups having two or more available bonding sites and are linked to one another through covalent bonds in polymer molecule. Most polymers can be described in terms of their structural unit or units. The units can be arranged and connected in a variety of ways. In the most straightforward type of polymer , the linear polymer , the units are connected to one another in the chain arrangement such as :

$X — M — M — M — M \ldots Y$ or $X —(M)_n— Y$,

where M is a structural unit or a monomer and n is the degree of polymerization. The degree of polymerization (DP) describes the molecular size . High molecular weight polymers, especially synthetic polymers, have varying degrees of polymerization or a molecular weight distribution among the chains within an individual polymer batch. The chain of structural units M is termined on either end by X and Y , whereas M must be at least bivalent (two bonding sites) , X and Y , the end groups, are monovalent (one bonding site). X and Y may be identical or different. On the other hand, the structural recurring unit may be trivalent (tri-functional) or polyvalent (polyfunctional) . Polymers made up of there units can have nonlinear or branched structure. At least some of the units must be trivalent for a branched molecule. Polymer molecule such as that depicted can be interconnected to have a network structure, which may be planar network or a three-dimensional space network.



A polymer of this form, in which the structural units of the side chain are identical to those of the main chain (or back-bone),is said to be branched. If the side chain of a branched polymer are formed from structural units which are different from those of the backbone, the polymer is a graft copolymer. The presence of trifunctional units in a polymer chain allows wide variations in molecule geometry, for example, a side chain in a branched polymer may be terminated either with a monofunctional end-group, or by reaction with trifunctional unit in another chain. In the latter case two chains become joined by a crosslink. If crosslinking becomes extensive, the polymer forms networks which may be two- or three-dimensional. The formation of three-dimensional networks during polymerization results in a cross-linked networks which forms a gel fraction, insoluble in solvents appropriate for the noncrosslinked material, whilst the remaining soluble, branched but uncrosslinked material forms a soluble fraction. The conversion at which gel formation occurs is termed the gel point. In dealing with highly crosslinked polymers, the concept of molecular weight becomes increasingly meaningless and, at high degrees of crosslinking, the entire polymer sample may be regarded as a single molecule. Poly (ethylene adipate) is an example of linear polymers,



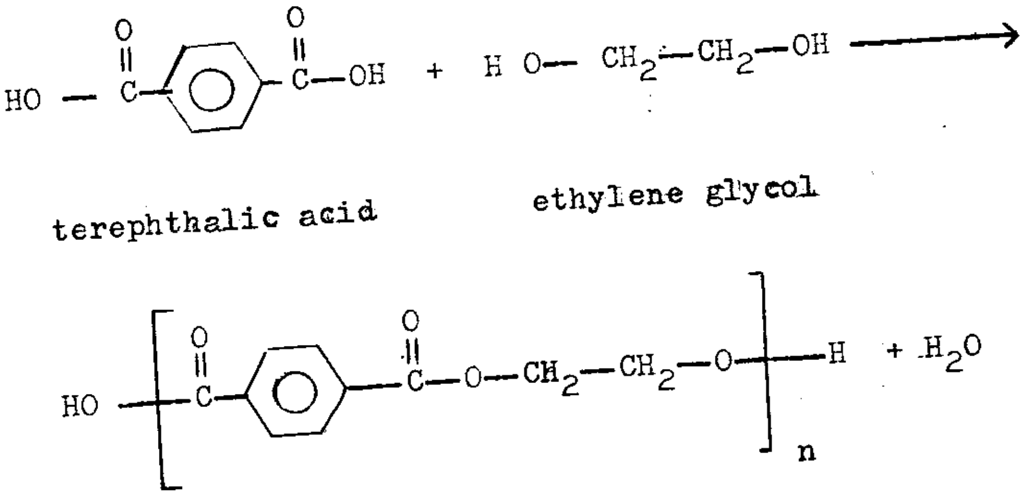
$$n\,HO-(CH_2)_2-OH + n\,HOOC-(CH_2)_4-COOH \longrightarrow H\left[O-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n OH + n\,H_2O$$

In this example, water has been lost, and recurring unit consists of two different structural units. In many cases the elementary analysis will not distinguish end groups in a high molecular weight compound. Even end groups in different polymer chains from the same polymerization reaction can be different.

2. Polymer Classification:

Carothers recognized the need for classification of polymers and divided all polymers into two types : condensation polymers and addition polymers(2), as follows:

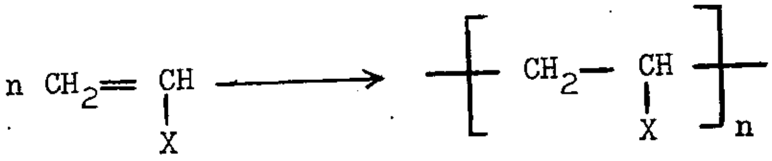
i- Condensation polymerization involves the reaction of polyfunctional molecule or molecules with loss of some simple molecule such as water, hydrogen chloride and methanol with formation of macromolecule. When a difunctional molecule is used, a linear condensation takes place. Typical of condensation polymers are polyesters, polyamides and polyurethanes. For example, a polyester is formed by typical condensation reaction between bi-functional monomers, with the elemination of water.



terephthalic acid ethylene glycol

poly(ethylene terephthalate)

ii- An addition polymerization is one in which the recurring units have the same composition as the monomer or monomers from which they were formed(1). The polymer is formed from a bi- or polyfunctional monomer by the addition of one monomer to another without the loss of any portion of the monomer. Polymers formed from the polymerization of vinyl monomers are the most common of this class:



$$n\ CH_2{=}\underset{|\atop X}{CH} \longrightarrow \left[CH_2 - \underset{|\atop X}{CH} \right]_n$$

Addition polymerization of vinyl monomers to give high molecular weight polymers proceeds by a chain mechanism. Whether the mechanism is of a free radical, cationic, or anionic type, this polymerization features an active site at the end of the growing polymer chain.

3. Free Radical Addition Polymerization :

Free radical addition polymerization is a very powerful method for the preparation of polymer from a wide variety of unsaturated vinyl, vinylidene and diene monomers and is one of the most widely used industrial method for the manufacture of addition polymers(3). The essential reaction in addition polymerization is :

$$n\ M \longrightarrow M_n$$

n representing the average number of monomer molecules which join together to form a polymer molecule. Since this number is usually very large, a polymer molecule must be formed by the following series of consecutive reactions:

$$\begin{aligned}
M_1^* + M &\longrightarrow M_2^* \\
M_2^* + M &\longrightarrow M_3^* \\
M_3^* + M &\longrightarrow M_4^* \\
&\ \ \vdots \\
M_i^* + M &\longrightarrow M_{i+1}^*
\end{aligned}$$

In this representation of the growth process, M_i^* stands for a polymer molecule containing i monomer units which is potentially capable of reacting with a monomer molecule. These polymeric active centers , as they are called, may or may not be identical with the final polymer produced; this depends simply on the specific chemical nature of the active centers and on the reaction conditions. In a free radical polymerization the following reactions should be considered:

i- reaction which lead to the propagation of the free radical capable of reaction with monomers.

ii- the reaction already outlined in which monomer molecules add successively to radical active centers with the formation of further radicals.

iii-reaction by which the radicals are destroyed with the production of polymer unreactive towards monomer.

These three reactions are referred to as initiation, propagation and termination reactions respectively, and the whole process is an example of a wider class of reaction known as chain reaction as follows :

i- Initiation:

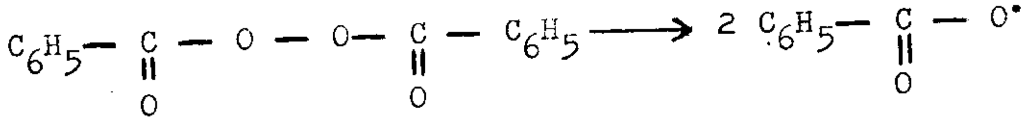
The usual procedure employed to produce the radical containing one monomer unit is to add to the monomer a substance or substances which produce radicals capable of reacting with it . These additives are termed initiators, the reaction being the composite process .

$$I \longrightarrow \alpha R^{\bullet}$$

$$R^{\bullet} + M \longrightarrow M_1$$

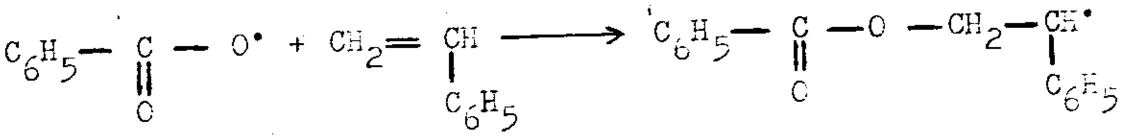
Where I represents the initiator, $R^{\bullet}$ the radical produced therefrom and α the number of such radicals obtained; the presence of the dot to the right of a symbol indicates an unpaired electron and its radical nature.

Probably the most widely used initiators are the organic peroxides and azo compounds. These substances decompose spontaneously into free radical in the common organic solvents at a finite rate at temperature between 50 and 140°C, for example, benzoyl peroxide in benzene at 60°C decomposes into two benzoloxy radicals by simple scission of the weak peroxy bond.



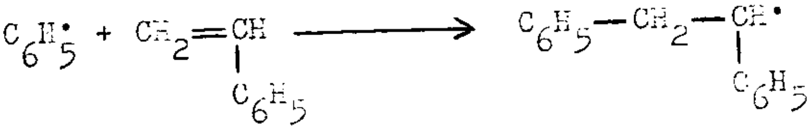
$$C_6H_5-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-C_6H_5 \longrightarrow 2\ C_6H_5-\underset{\underset{O}{\|}}{C}-O^{\bullet}$$

The benzoyloxy radicals so produced may either decompose to give a phenyl radical and CO_2 or they may undergo reaction with solvent or further benzoyl peroxide. In the presence of vinyl monomer, these latter reactions are unimportant, most of the benzoloxy or phenyl radicals react with the monomer, thus in the case of styrene :



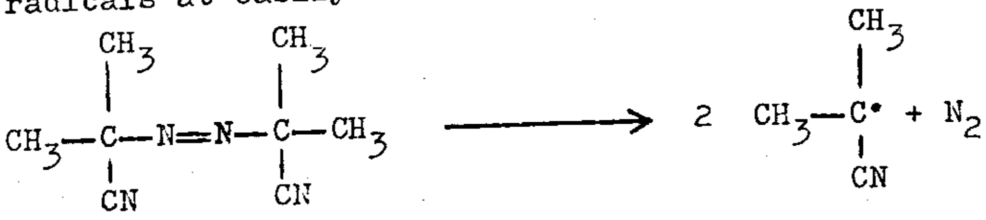
$$C_6H_5-\underset{\underset{O}{\|}}{C}-O^{\bullet} + CH_2=\underset{\underset{C_6H_5}{|}}{CH} \longrightarrow C_6H_5-\underset{\underset{O}{\|}}{C}-O-CH_2-\underset{\underset{C_6H_5}{|}}{CH^{\bullet}}$$

or



$$C_6H_5^{\bullet} + CH_2=\underset{\underset{C_6H_5}{|}}{CH} \longrightarrow C_6H_5-CH_2-\underset{\underset{C_6H_5}{|}}{CH^{\bullet}}$$

Another example is afforeded by the azo **compounds**, **azo-bis-isobutyronitrile (AIBN)** which similry decomposes into radicals at easily accessible temperature :

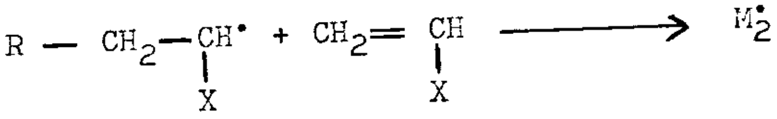


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}-N=N-\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}-CH_3 \longrightarrow 2\ CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C^\bullet}} + N_2$$

These radicals react with monomers in an exactly similar way to that described for benzoyloxy or phenyl radicals.

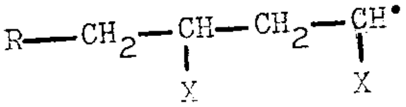
ii-Propagation :

Free radical chain propagation proceeds by the rapid addition of monomer molecules to the active radicals generated in the initiation step. The process is repeated as many more propagate the reactive center. If we write out the first reaction in more detail for the case where M represents a vinyl monomers.



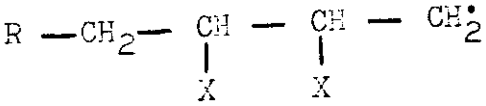
$$R-CH_2-\underset{\underset{X}{|}}{CH^\bullet} + CH_2=\underset{\underset{X}{|}}{CH} \longrightarrow M_2^\bullet$$

The radical $R-CH_2-\underset{\underset{X}{|}}{CH^\bullet}$ attaches itself to the CH_2 group of the reacting monomer or to the CH —X group to produce what is termed the "head to tail" or "head to head" arrangement as follows:



$$R-CH_2-\underset{\underset{X}{|}}{CH}-CH_2-\underset{\underset{X}{|}}{CH^\bullet}$$

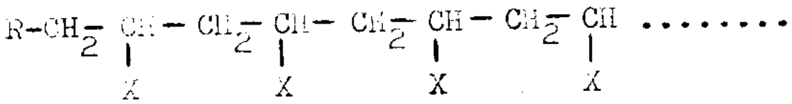
"head to tail"



$$R-CH_2-\underset{\underset{X}{|}}{CH}-\underset{\underset{X}{|}}{CH}-CH_2^\bullet$$

"head to head"

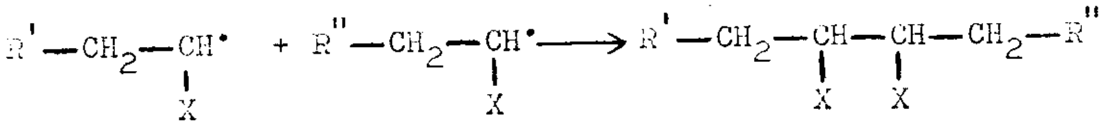
Of course, a few "head to head" additions will take place during the growth of the polymer depending on the magnitude of the activation energy difference between the two reactions producing the alternative forms. For practical purposes, the ordinary vinyl polymer produced is considered to consist predominantly of monomer units arranged in a "head to tail" fashion.



$$R{-}CH_2{-}\underset{\underset{X}{|}}{CH}{-}CH_2{-}\underset{\underset{X}{|}}{CH}{-}CH_2{-}\underset{\underset{X}{|}}{CH}{-}CH_2{-}\underset{\underset{X}{|}}{CH}\ \ldots\ldots\ldots$$

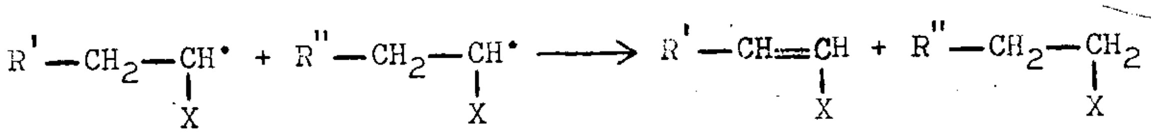
iii- Termination :

The radical must be destroyed in a reaction system by a bimolecular process since their disappearance involves spin pairing. There are two ways of achieving this result. Firstly, two radicals can simply combine together according to the eqation:



$$R'{-}CH_2{-}\underset{\underset{X}{|}}{CH^{\bullet}} + R''{-}CH_2{-}\underset{\underset{X}{|}}{CH^{\bullet}} \longrightarrow R'{-}CH_2{-}\underset{\underset{X}{|}}{CH}{-}\underset{\underset{X}{|}}{CH}{-}CH_2{-}R''$$

This process is termed combination termination and results in the formation of a "head-to-head" linkage. Alternatively, a hydrogen atom can be transferred from one radical to the other giving two polymer molecules, one saturated and the other possessing an olefinic double bond at one end, this process being termed disproportionation termination.

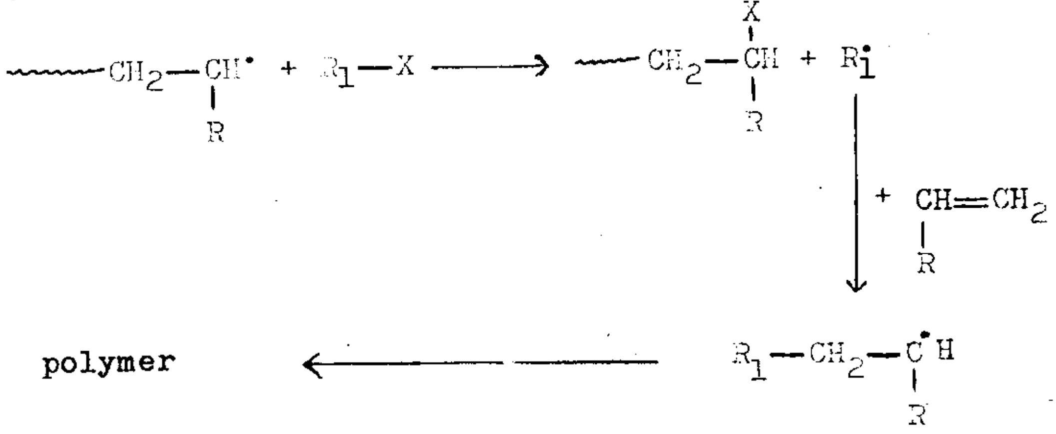


$$R'{-}CH_2{-}\underset{\underset{X}{|}}{CH^{\bullet}} + R''{-}CH_2{-}\underset{\underset{X}{|}}{CH^{\bullet}} \longrightarrow R'{-}CH{=}\underset{\underset{X}{|}}{CH} + R''{-}CH_2{-}\underset{\underset{X}{|}}{CH_2}$$

It should be noted that in combination termination a polymer with two initiation fragments per molecule is produced, but disproportionation produced a polymer molecule with a single initiation end group.

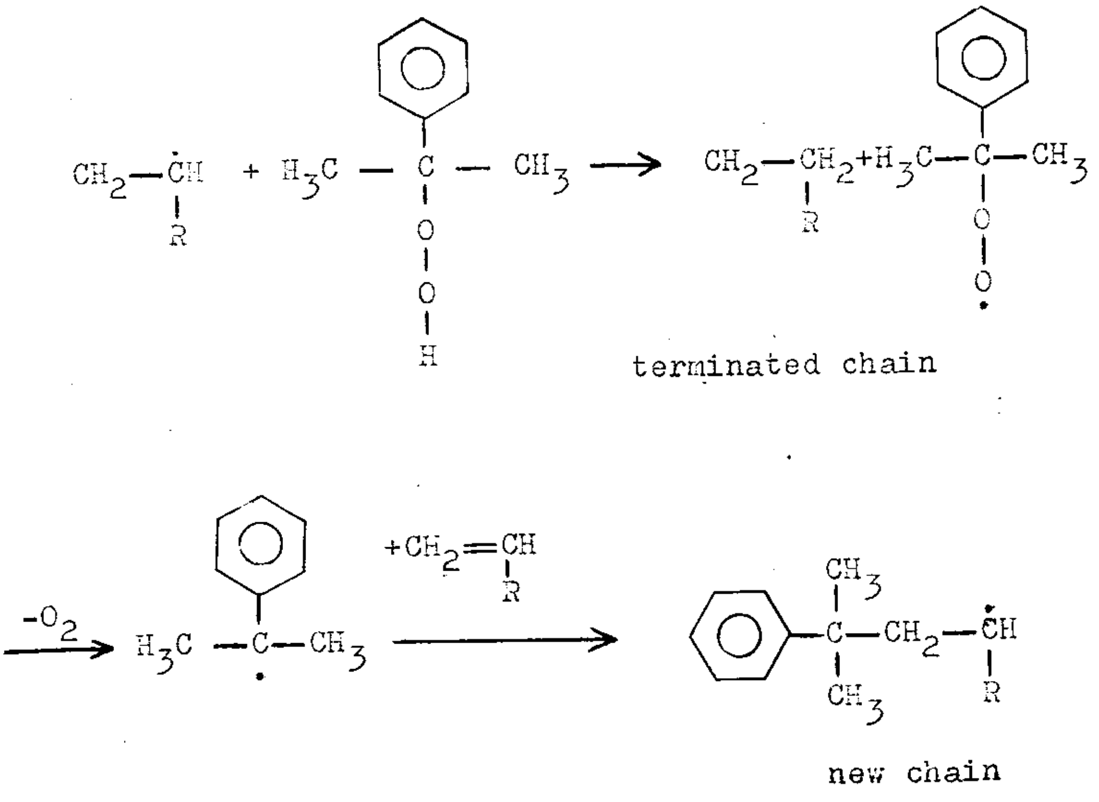
Chain Transfer:

A growing chain radical may abstract an atom (for example,hydrogen or chlorine) from another molecule and thus become saturated, and the molecule from which the atom has been abstracted will then become a radical and start a new chain(4). The chain reaction therfore continues, even through the chain growth of the first macromolecule has stopped; i.e., it has transferred the reaction chain to another molecule . This reaction is therefore called a transfer reaction, or just chain transfer .



Chain transfer of this type may occur with the initiate, with the monomer, with the solvent or other compounds which have been added in order to promate chain transfer (modifiers), and with growing or complete polymer chains .

Among the common initiators, the hydroperoxides (for example, t-butyl-hydroperoxide and cumene-hydroperoxide) are the ones with a tendency to transfer reactions, whereas benzoylperoxide, and especially azo-bis-isobutyronitrile, do not take part in transfer reactions. In the transfer reactions, the initiator molecule reacts with a chain radical to determinate it and at the same time gives rise to another radical which then starts a new-chain:



This type of decomposition of the initiator by a growing chain radical (induced decomposition) must be considered in addition to the spontaneous decomposition. Since such an induced decomposition forms as many new radicals as it consumes, the radical concentration remains unaffected.

4- Free radical copolymerization:

Free-radical copolymerization may be defined as a process where-by two or more monomers are integral parts of a high polymer via radical chain reaction. A copolymer is the product resulting from such a process. The importance of the free-radical copolymerization, is a method for modifying the properties of polymers. Hard polymers, as for example, polyvinyl chloride, can be made softer, by copolymerization with monomer where homopolymers are rubber like, such as vinyl ether or acrylic acid esters. There is a series of monomers, such as maleic anhydride, the fumarates, the maleates, and vinyl ethers, which by themselves do not polymerize or only slowly by radical mechanisms, are often used as components of copolymerization and then copolymerize by a radical mechanism. Copolymerization is one of the most important as well as the most obvious way of introducing variety into the structure of copolymers.

i- Copolymerization composition equation

It is assumed that the rate of addition of any monomers to the free end on the chain depends on the nature of the end group bearing the radical, that is, where monomers M_1 and M_2 give M_1 and M_2 ends, the following set of equations can be writtem for the various types of addittion possible(4&5)

$$\sim\!M_1^{\bullet} + M_1 \xrightarrow{k_{11}} \sim\!M_1M_1^{\bullet} \qquad \text{rate} = k_{11}[M_1^{\bullet}]\,[M_1] \qquad (1)$$

$$\sim\!M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim\!M_1M_2^{\bullet} \qquad \text{rate} = k_{12}[M_1^{\bullet}]\,[M_2] \qquad (2)$$

$$\sim\!M_2^{\bullet} + M_2 \xrightarrow{k_{22}} \sim\!M_2M_2^{\bullet} \qquad \text{rate} = k_{22}[M_2^{\bullet}]\,[M_2] \qquad (3)$$

$$\sim\!M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \sim\!M_2M_1^{\bullet} \qquad \text{rate} = k_{21}[M_2^{\bullet}]\,[M_1] \qquad (4)$$

where k_{11} is the rate constant for the reaction in which monomer M_1 adds to a radical chain ending in M_1 , k_{12} is the rate constant for the reaction in which monomer M_2 adds to a radical chain ending in M_1...... etc.If a steady state is reached instantly after the polymerization is started, then the total concentration of $M_1^{\bullet}$ and $M_2^{\bullet}$ will remain constant, and the rate of conversion of $M_1^{\bullet}$ to $M_2^{\bullet}$ will equal the rate of conversion of $M_2^{\bullet}$ to $M_1^{\bullet}$:

$$k_{21}\,[M_2^{\bullet}]\,[M_1] = k_{12}[M_1^{\bullet}][M_2]$$

The rate of disappearance of the two different monomer types can be expressed as :

$$-d\,M_1 \,/\, dt = k_{11}[M_1^{\bullet}]\,[M_1] + k_{21}\,[M_2^{\bullet}]\,[M_1] \qquad (5)$$

$$-d\,M_2 \,/\, dt = k_{12}[M_1^{\bullet}][M_2] + k_{22}\,[M_2^{\bullet}]\,[M_2] \qquad (6)$$

if k_{11}/k_{12} and k_{22}/k_{21} are defined as r_1 and r_2 respectively, then:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^\cdot][M_1] + k_{21}[M_2^\cdot][M_1]}{k_{12}[M_1^\cdot][M_2] + k_{22}[M_2^\cdot][M_2]}$$

$$= \frac{[M_1]}{[M_2]}\left[\frac{k_{11}[M_1^\cdot] + k_{21}[M_2^\cdot]}{k_{12}[M_1^\cdot] + k_{22}[M_2^\cdot]}\right]$$

Multiplying by $[M_2] / k_{21}[M_1]$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{\dfrac{k_{11}}{k_{21}}\dfrac{[M_1^\cdot][M_1]}{[M_2^\cdot]} + [M_2]}{\dfrac{k_{12}}{k_{21}}\dfrac{[M_1^\cdot][M_2]}{[M_2^\cdot]} + \dfrac{k_{22}}{k_{21}}[M_2]}\right)$$

since $[M_1] = \dfrac{k_{12}}{k_{21}}\dfrac{[M_1^\cdot][M_2]}{[M_2^\cdot]}$, then

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}\right) \qquad (7)$$

This equation relates the copolymer composition to comonomer concentration in the feed. The copolymerization equation can also be rearranged in terms of mole fraction instead of concentration as(7):

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + 2 f_2^2} \qquad (8)$$

where F_1 = mole fraction of monomer M_1 in copolymer, and

f_1 = mole fraction of monomer M_1 in feed.

ii- Types of copolymerization behaviour :

From the copolymerization equations (1-4) , if $K_{11} > k_{12}$ and $k_{22} > k_{21}$ copolymerization would be insignificant and a mixture of homopolymers or copolymer should be obtained, while if $k_{12} > k_{11}$ and $k_{21} > k_{22}$ this will lead to the formation of copolymer with an alternating sequence . If $k_{12} = k_{11}$ and $k_{21} = k_{22}$, the frequency with which M_1 or M_2 add to the chain end is determined by their concentration leading to an ideal copolymerization . Their copolymerization can also be classified on whether the product of the two monomer reactivity ratios r_1r_2 is unity, less than unity, or greater than unity as follows :

a- when $r_1r_2 = 1$, the two types of propagation species $M_1^{\cdot}$ and $M_2^{\cdot}$ show the same preference for adding one or the other of the two monomers, and the monomer unit will be incorporated in a random manner influenced by the feed composition . Thus, substituting $r_2 = 1/r_1$ in equation (7) and (8) one get :

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \qquad (9)$$

and

$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2} \qquad (10)$$

b- when $r_1r_2 < 1$, this is the case when r_1r_2 decreases from unity to zero . Most radical copolymerization lie between the two extremes of ideal and alternating behaviour . The alterntion is measured by the tendency of r_1r_2 product to approach zero . In this case, when r_1 and r_2 are both less than unity, the copolymerization shows azeotropic composition at which the copolymer and the feed composition are the same, and the copolymerization occurs without change in the feed composition to give :

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \qquad (11)$$

by substitution in equation (8) one gets:

$$F_1 = f_1 = \frac{1 - r_2}{2 - (r_1 + r_2)} \qquad (12)$$

c- when $r_1 r_2 > 1$, this is a rare case and if it exists, it leads to the synthesis of blocks of copolymer or a mixture of the homopolymers .

iii- Methods of calculating monomer reactivity ratios :

Actual numerical values of the reactivity ratios are determined from experimental measurements of the molar ratios of the monomers in the copolymer that is formed from reactant mixtures of known initial monomer concentration ratios (8).The techniques used for quantative determination of copolymer composition include elemental analysis, radioisotopic labelling. and ultraviolt, infrared and nuclear magnatic spectroscopy . All procedures depend on copolymerization carried out to low degrees of conversion (less than 10%)and the experimental data can be analyzed in several ways. The more established procedures involving determination of monomer reactivity ratios are :

a- Intersection method

This method originated by Mayo and Lewis(6), depend on the deriving r_1 and r_2 from suitable composition data consists in substituting the copolymer and monomer composition for a single copolymerization in the equation 7 page (14) which can be expressed in terms of molar ratios insted of concentration as(4) :

$$b = \frac{r_1 a + 1}{r_2 / a + 1} \qquad (13)$$

where a and b are the molar ratios of the comonomers in the feed and copolymer, respectively . In this method r_2 is plotted as a function of r_1 . This is done for each of several copolymerization . If there were no experimental error , all the lines would intersect at the same point, which would reresent the proper values of r_1 and r_2 . An average point of intersection is taken to represent the experimental r_1 and r_2 values .

b- Joshi-Kapur method (9)

In this method, the inherent experimental error in the chemical analysis can be interpreted precisely by defining limits of corresponding probable error in r_1 and r_2 values by procedure adopted by Lewis et al (6) . But the locating of the best of intersection from the "probable area" confind by the different straight lines on the r_1 , r_2 plot . The coordinates of the point of intersection (r_1, r_2) and the tangent value of the angle of intersection $(\tan \theta)$ are calculated . Form the following two equation of the intersecting lines given by the general copolymer composition (for low conversion) equation(6) .

$$r_2 = \left[\left(\frac{M_1}{M_2} \right)^2 \frac{m_2}{m_1} \right] r_1 + \frac{M_1}{M_2} \left(\frac{m_2}{m_1} - 1 \right)$$

$$r_2 = \left[\left(\frac{M'_1}{M'_2} \right)^2 \frac{m'_2}{m'_1} \right] r_1 + \frac{M'_1}{M'_2} \left(\frac{m'_2}{m'_1} - 1 \right)$$

Therefore:

$$r_1 = \frac{\left[\frac{M'_1}{M'_2} \left(\frac{m'_2}{m'_1} - 1 \right) \right] - \left[\frac{M_1}{M_2} \left(\frac{m_2}{m_1} - 1 \right) \right]}{\left[\left(\frac{M_1}{M_2} \right)^2 \frac{m_2}{m_1} \right] - \left[\left(\frac{M'_1}{M'_2} \right)^2 \frac{m'_2}{m'_1} \right]}$$

and

$$\tan \theta = \frac{\left[\left(\frac{M_1}{M_2} \right)^2 \frac{m_2}{m_1} \right] - \left[\left(\frac{M'_1}{M'_2} \right)^2 \frac{m'_2}{m'_1} \right]}{1 + \left[\left(\frac{M_1}{M_2} \right)^2 \frac{m_2}{m_1} \right] \left[\left(\frac{M'_1}{M'_2} \right)^2 \frac{m'_2}{m'_1} \right]}$$

where M_1 / M_2 and M'_1 / M'_2 are any two initial monomer concentration ratios and m_1 / m_2 and m'_1 / m'_2 are the corresponding ratios in the copolymer . The value of r_1 and r_2 are multiplied by tangents of the angle of intersection and summed up . This sum divided by the sum of the tan θ values gives the necessary average as shown below :

$$\overline{r}_1 = \frac{\sum r_1 \tan\theta}{\sum \tan\theta} \quad \text{and} \quad \overline{r}_2 = \frac{\sum r_2 \tan\theta}{\sum \tan\theta}$$

c- Fineman-Ross method

The method of Fineman and Ross(10) represents a considerable improvement in the direction of straightforward analysis of copolymerization data . This is done by solving equation (13) for r_2 and r_1 in the form :

$$a - \frac{a}{b} = r_1 \frac{a^2}{b} - r_2$$

$a - a / b$ is then plotted aganist a^2 / b and a straight line is drawn through the points, using the method of least squares . The intercept and slope of the line are equal to $-r_2$ and r_1 respectively .

d- Tidwell-Mortimer method

In detailed critical treatises, Tidwell and Mortimer(11) pointed out the defects of the different method and suggested a saturated computerized procedure; thd nonlinear least square method . This method presumes that there is no possible experimental error in the independent variable; the monomer composition of the feed; and the absolute error in the copolymer composition is independent of its value or constant.

e- Yezrielev-Brokhina-Roskin method

Yezrielev, Brokhina and Roskin(12) transformed the linear equation of copolymer composition into symmetrical form as :

$$a / b^{\frac{1}{2}} \cdot r_1 - b^{\frac{1}{2}} / a \cdot r_2 + (1 / b^{\frac{1}{2}} - b^{\frac{1}{2}}) = 0$$

where $a = M_1 / M_2$ (molar ratios of the two monomers in the comonomer mixture)

and $b = m_1 / m_2$ (molar ratios of the two monomer in the copolymer)

In this method the theoretical line is situated evenly between the experimental points of positive and negative error which leads to determination of reactivity ratios more accurate.

f- Kelen-Tüdős method

The method recently proposed by Kelen and Tüdős(13) show to be most reliable form of differential methods based on the monomer feed-copolymer composition equation, in as much as the differential equation is applicable for the system. Like other differential methods, the Kelen-Tüdős equations obviously suitable for low-conversion data . This equation based on a new graphically valuable linear equation as follows :

$$\eta = (r_1 + r_2/\alpha) \xi - (r_2/\alpha)$$

where $\eta = \frac{a(b-1)}{b + a^2}$, $\varepsilon = \frac{a^2}{b + a^2}$

and

$$\alpha = \frac{a_{min} \times a_{max}}{(b_{min} \times b_{max})^{\frac{1}{2}}}$$

The variable ξ cannot take any positive value, only those in interval 0 – 1 . Thus, plotting the η values in the function of $\xi = 0$ and $\xi = 1$ give $-r_2/\alpha$ and r_1 , respectively (both as intercepts) .

iv- Factors affecting monomer reactivity ratios :

With respect to free-radical copolymerization it may stated that reactivity ratios are comparatively little influenced by most common variables such as conversion, solvent and method of polymerization(14). In the range of temperature from room temperature to about 100 °C there is little variation in reactivity ratios in binary copolymerization . However, there is tendency for r_1r_2 product to approach 1 as temperature increases . Copolymerization has been affected at temperature as – 70 °C and temperature as high as 130 °C, with large change in reactivity ratios . With respect to the solvent, numerous studies have been made which indicate that a change of solvent has a little effect on monomer reactivity ratios. Accordingly, a highly polar or nonpolar solvent, does not appear to influence the value of reactivity ratios . The effects of dilution on reactivity ratios have been studied and it has been concluded that no substantial effect exists. Also, polymerization by solvent-nonsolvent techniques gives reactivity ratios similar to those of homopolymers system, that is the precipitation of copolymer during polymerization does not alter reactivity ratios . Monomer reactivity ratios have also been found to vary with pressure, for example, copolymerization of methyl methacrylate and acrylonitrile(15), the product of r_1r_2 increased from 0.16 (at atmospheric pressure) to 0.91 (at 1000 atmosphere) indicating that increased pressure increases the tendency for this system towards blocks .

v- Monomer reactivity and interpretation by Q-e scheme :

The monomer reactivity ratio values , r_1 and r_2 , describe the relative tendency of two monomers to add to a particular growing chain(16) The reactive end of the growing chain is a free radical derived from one of the two monomers "and two types of reactive ends can exist" .Because the values obtained experimentally are relative values, they pertain only to one particular pair of monomers . Several correlation having varying degrees of complexty and theoretical formulation have been proposed .The best known and most widely used being the Alfrey-Price Q — e scheme . Q, is a measure of resonanse stabilization of monomer and corresponding radical, (describes the reactivity of monomer), and e, describes the polarity interaction of radical and molecule . The relationship between these parameters and actual reactivity ratios was proposed to be :

$$r_1 = \frac{k_{11}}{k_{12}} = \left(\frac{Q_1}{Q_2}\right)\left[\exp \; -e_1\,(e_1 - e_2\,)\right] \tag{14}$$

$$r_2 = \frac{k_{22}}{k_{21}} = \left(\frac{Q_2}{Q_1}\right)\left[\exp \; -e_2\,(e_2 - e_1\,)\right] \tag{15}$$

$$r_1 r_2 = \exp \; -(\,e_1 - e_2\,)^2 \tag{16}$$

$$\ln r_1 r_2 = -\,(\,e_1 - e_2\,)^2 \tag{17}$$

Price choose styrene as the standard monomer with the value $Q = 1$ and $e = -0.8$. The Q and e values of any monomer that has been copolymerized with styrene can be calculated from r_1 and r_2 values given in literature . Conversely, knowing the Q and e for any two monomers the r_1 and r_2 values can be calculated for monomer pair, whether or not they have ever been copolymerized . While the predicted behaviour is not always exactly like the experimental result, the Alfry-Price scheme nevertheless leads at least to a good approximation . The major shortcoming of the Q – e scheme is that all radical polymerizations involve not only resonance and polar factors, but also steric factors. It is certainly conceded that steric factors limit the applicability of the scheme which is an empirical method of correlation.

vi- Distribution of monomers in copolymers :

Although chemical analysis of copolymers indicates the molar ratios of monomers present , it does not reveal the monomer in which the monomer units are distributed in the copolymer . The distribution of the monomer units along a chain will cover the range from complete randomness in the "ideal" copolymer to strict alternation in the "alternating" copolymer . Expression for the "ideal" case where developed by Wall,(17&18) and general expressions for value of the monomer reactivity ratios by Alfrey and Goldfinger(5), as shown by the latter outhors, but in the symbols used here, for long chains the probability P_{11} of an $M_1^{\cdot}$ radical adding M_1 and P_{12} is the probability of an $M_1^{\cdot}$ radical adding M_2...etc. The fractions of the six triad types can be calculated as follows :

$$P_{11} = (1 + m_2 / r_1 m_1)^{-1} \qquad (18)$$

$$f_{111} = P_{11}^2 \qquad (19)$$

$$P_{12} = (1 + r_1 m_1 / m_2)^{-1} \qquad (20)$$

$$f_{212} = P_{12}^2 \qquad (21)$$

$$f_{112} = 2P_{12} (1 - P_{12}) \qquad (22)$$

$$P_{22} = (1 + m_1 / r_2 m_2)^{-1} \qquad (23)$$

$$f_{222} = P_{22}^2 \qquad (24)$$

$$P_{21} = (1 + r_2 m_2 / m_1)^{-1} \qquad (25)$$

$$f_{121} = P_{21}^2 \qquad (26)$$

$$f_{221} = 2P_{21} (1 - P_{21}) \qquad (27)$$

The sequence distributions of the monomer units along the copolymer chains were calculated from the monomer reactivity ratio basis of terminal. copolymerization model(13). the variation in sequence distribution of the triad are represents as: f_{111} , f_{212} , f_{112} , f_{222} , f_{121} , and f_{221} .

vii- Terpolymer composition equation :

The extensive work of many investigators has coverd the field of two component polymers so thoroughly that the possibility of preparing new compositions of this type is unlikely except as new monomers become available . In contrast, the much large field of three component polymers (terpolymers) still provides many possibilities for new compositions. These polymers have received relatively little attention possibly because general property composition relationships have not, as yet been publicized(19). The study of three component systems was discovered by which a range of high-clarity temperatures could be located easily in many three-component systems . This method has been extended to four and five component systems and has provided a more systematic approach to the study of multicomponent polymers . It has been shown by Alfery and Goldfinger(20) that there are nine propagation reaction in determination terpolymer composition .

$$\begin{array}{l|l|l}
\sim \dot{M}_1 + M_1 \xrightarrow{k_{11}} \sim M_1 - \dot{M}_1 & \sim \dot{M}_2 + M_1 \xrightarrow{k_{21}} \sim M_2 - \dot{M}_1 & \sim \dot{M}_3 + M_1 \xrightarrow{k_{31}} \sim M_3 - \dot{M}_1 \\
\sim \dot{M}_1 + M_2 \xrightarrow{k_{12}} \sim M_1 - \dot{M}_2 & \sim \dot{M}_2 + M_2 \xrightarrow{k_{22}} \sim M_2 - \dot{M}_2 & \sim \dot{M}_3 + M_2 \xrightarrow{k_{32}} \sim M_3 - \dot{M}_2 \\
\sim \dot{M}_1 + M_3 \xrightarrow{k_{13}} \sim M_1 - \dot{M}_3 & \sim \dot{M}_2 + M_3 \xrightarrow{k_{23}} \sim M_2 - \dot{M}_3 & \sim \dot{M}_3 + M_3 \xrightarrow{k_{33}} \sim M_3 - \dot{M}_3
\end{array}$$

The rate of disappearance of individual monomers may be expressed as :

$$- d\,M_1/dt = k_{11}[M_1^{\bullet}][M_1] + k_{21}[M_2^{\bullet}][M_1] + k_{31}[M_3^{\bullet}][M_1]$$

$$- d\,M_2/dt = k_{12}[M_1^{\bullet}][M_2] + k_{22}[M_2^{\bullet}][M_2] + k_{32}[M_3^{\bullet}][M_2]$$

$$- d\,M_3/dt = k_{13}[M_1^{\bullet}][M_3] + k_{23}[M_2^{\bullet}][M_3] + k_{33}[M_3^{\bullet}][M_3]$$

In a manner completely analogous to that described for two monomer systems (page 13) the terpolymerization composition equation, which relates the instantaneous terpolymer composition to the feed of monomers (using the assumption of a steady state), could be obtained as :

$$\begin{aligned} d[M_1]:d[M_2]:d[M_3] = {} & M_1\left[\frac{[M_1]}{r_{31}r_{21}}+\frac{[M_2]}{r_{21}r_{32}}+\frac{[M_3]}{r_{31}r_{23}}\right]\left[[M_1]+\frac{[M_2]}{r_{12}}+\frac{[M_3]}{r_{13}}\right] \\ & : M_2\left[\frac{[M_1]}{r_{12}r_{31}}+\frac{[M_2]}{r_{12}r_{32}}+\frac{[M_3]}{r_{32}r_{13}}\right]\left[[M_2]+\frac{[M_1]}{r_{21}}+\frac{[M_3]}{r_{23}}\right] \\ & : M_3\left[\frac{[M_1]}{r_{13}r_{21}}+\frac{[M_2]}{r_{23}r_{12}}+\frac{[M_3]}{r_{13}r_{23}}\right]\left[[M_3]+\frac{[M_1]}{r_{31}}+\frac{[M_2]}{r_{32}}\right] \end{aligned} \qquad \text{---(28)}$$

The r values shown in this equation are r_1 and r_2 values of the three monomer pairs M_1-M_2, M_2-M_3 and M_1-M_3. In order to distinguish these better, each r value has now two index numbers :

$M_1 - M_2$	$M_2 - M_3$	$M_1 - M_3$
$r_1 = k_{11}/k_{12} = r_{12}$	$r_1 = k_{22}/k_{23} = r_{23}$	$r_1 = k_{11}/k_{13} = r_{13}$
$r_2 = k_{22}/k_{21} = r_{21}$	$r_2 = k_{33}/k_{32} = r_{32}$	$r_2 = k_{33}/k_{31} = r_{31}$

Terpolymerization composition equation has been tested by a number of workers and has been found to describle experim- experimental copolymerization within the limits to be expected from the accuracy of the reactivity values$^{(21-23))}$.

Ham$^{(24)}$ proposed a simler expression for the terpolymer composition equation when polar and steric effects are absent or when polar effects between the various radicals and monomers are similar so that :

$$r_{12}\, r_{23}\, r_{31} = r_{13}\, r_{32}\, r_{21} \tag{29}$$

and the terpolymer composition equation was simplifed in the form:

$$\begin{aligned} d[M_1] : d[M_2] : d[M_3] &= M_1 \left[M_1 + \frac{M_2}{r_{12}} + \frac{M_3}{r_{13}} \right] : \\ &= M_2 \frac{r_{21}}{r_{12}} \left[\frac{M_1}{r_{21}} + M_2 + \frac{M_3}{r_{23}} \right] : \\ &= M_3 \frac{r_{31}}{r_{13}} \left[\frac{M_1}{r_{31}} + \frac{M_2}{r_{32}} + M_3 \right] \end{aligned}$$

------------------------(30)

Mayo(25) reported that Ham's equation is potentially useful for bringing out inconsistencies between experimental data are theoretical correlations and prediction of behaviours of monomer in copolymerization. Also, Ham's probabilities are sometimes quite good and sometimes very poor.

Khan and Horowitz(26) studied the terpolymerization of vinyl acetate–dioctyl fumarate–N–vinyl pyrrolidone system and programmed the differential terpolymer composition equation on a digital computer in the following form:

$$
\begin{aligned}
&d\,M_1 : d\,M_2 : d\,M_3 = \\
&M_1 \left[M_1 r_{23} r_{32} + M_2 r_{31} r_{23} + M_3 r_{32} r_{21}\right]\left[M_1 r_{12} r_{13} + M_2 r_{13} + M_3 r_{12}\right] : \\
&M_2 \left[M_1 r_{32} r_{13} + M_2 r_{13} r_{31} + M_3 r_{12} r_{31}\right]\left[M_2 r_{21} r_{23} + M_1 r_{23} + M_3 r_{21}\right] : \\
&M_3 \left[M_1 r_{12} r_{23} + M_2 r_{13} r_{21} + M_3 r_{12} r_{21}\right]\left[M_3 r_{31} r_{32} + M_1 r_{32} + M_2 r_{31}\right]
\end{aligned}
\qquad \text{------------------------------(31)}
$$

Ring(27) studied the perdetermination of the copolymerization behaviour and the expected chemical heterogeneities is demonstrated for 2-and 3-component systems on the basis of calculations using the known of the statistical copolymerization. The existence of ternary azeotropes is discussed in connection with the system methyl methacrylate/glycidyl methacrylate/styrene.

Non azeotropic, but chemically homogeneous copolymers can principally be produced by continuous processes. The addition of a suitably selected monomer component may direct a copolymerization towards a greater chemical homogeneity of the product .

Ionic and corrdinative catalyst systems are also principally of producing statistical sequence distribution in copolymer molecule .

The terpolymer poly (styrene-co-acrylonitrile-co-styrylisocyanate)was syntherized(28)by radical initiation directly from styrene, acrylonitrile and cinnamoylazide . The monomer feed – terpolymer composition relationship was determined by Slocombe's triangular graph . The solubility, intrinsic viscosity, and melting range of the various terpolymers and the chemical reactions of the pendant isocyanate groups towards alcohol and amines were investigated .

The terpolymerization of acrylonitrile with styrene and 2 – 3 – dibromopropyl acrylate in emulsion and dimethyl formamide solution was investigated by Karia Saric(29) . Polymerization, when stopped at low conversions, yielded terpolymers that showed good agreement between experimental and theoretical copolymerization composition data, calculated from Alfrey – Goldfinger equation . The relationship between monomer feed and terpolymer composition is displayed on triangular coordinate graphs proposed by Slocombe . By using a computer program the lines of unique composition and binary azeotropic composition for both systems were established . In the case of emulsion polymerization the azeotropic ternary point was determined . The experimental results of emulsion terpolymerization fit the calculated curves satisfactory over a wide range of monomer compositions up to high conversions . The influence of 2,3 - dibromopropyl acrylate on the thermal and flammability characteristics of the terpolymers is described .

LITERATURE REVIEW

Itaconic acid is distinguished from maleic acid in being a vinylidene compound or an α-substituted acrylic acid. It has been homopolymerized employing potassium persulphate initiator to a molecular weight of 50.000(30). The failure of itaconic acid to homopolymerize to high molecular weights observed with acrylates is attributed to allylic hydrogen chain transfer with monomer, giving rise to a resonance stabilization radical. Poly-itaconic acid is even more soluble in water than the monomer, and produce solutions of relatively low viscosity . Poly-itaconic acid can also be prepared by polymerization of the monomer esters followed by hydrolysis . This is preferable to preparation via the diesters, since organic peroxide catalyzed bulk polymerization of the monoesters is substantially more rapid than polymerization of the esters . Emulsion copolymerization of styrene and itaconic acid were carried out in the conventional way, since the latter has a high solubility in water and a very low solubility in styrene(31) . All copolymerizations were allowed to proceed to low conversion (mainly $<4\%$) and this initial copolymer was isolated and purified . Copolymers of styrene with 10-70% dimethyl itaconate, and terpolymers with acrylonitrile, prepared in bulk with peroxide catalyst, resemble poly-methyl methacrylate but has better molding properties(32). Dialkyl itaconate copolymer with variety of acrylic monomers are reported to exhibit desirable physical properties . Levels of up to 30% dimethyl itaconate in methyl methacrylate casting syrups moderate the polymerization and suppress bubbling; flexural strength and hardness enhaced . The copolymerization of itaconic acid with most monomers, produce low molecular weight copolymers probably due to chain transfer. Copolymers of vinylidene chloride with itaconic acid and a third monomer acrylonitrile or an acrylic or methacrylic esters, are useful moisture proof and heat sealable coating media. Itaconic acid is also copolymerized in emulsion with lower alkyl acrylates for paper coating of improved adhesion. In equeous copolymerization of itaconic acid with acrylonitrile, the itaconate enters the polymer preferentially and retards the rate of copolymerization(33).

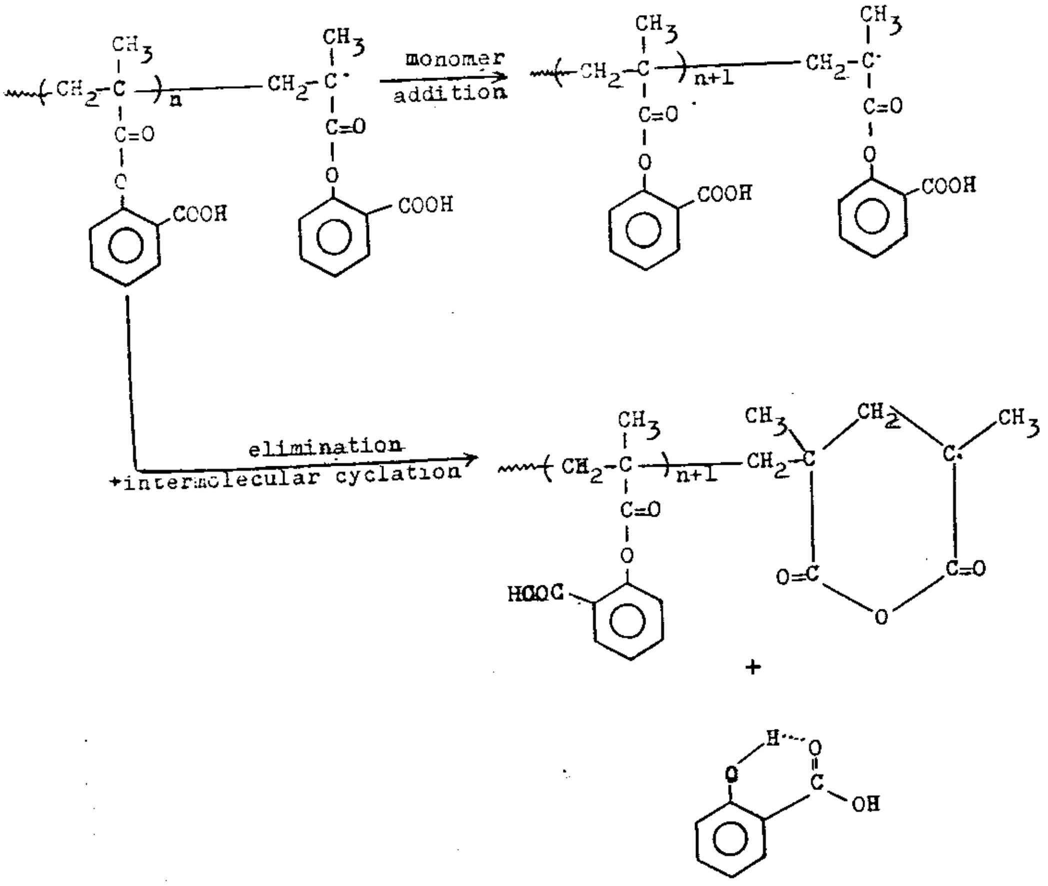
Homopolymerization of both mono-and di-alkyl esters of itaconic acid have been prepared and characterized(34) . polymers with esters side chain lengths varying from methyl to dodecyl were examined and found to exhibit a wide range of physical properties. While the property variation in these two series of homopolymers is extensive, it can be further expanded if esters with differing side chain lengths are polymerized . Velickovic et al.(35) prepared the three o-,m-,p- isomers of ditolyl itaconate by esterification of cresols and itaconic acid in presence of diphosphorous pentoxide, and then polymerized in bulk with AIBN as initiator . The polymers were investigated in dilute solution, and the results compared with those for poly(phenyl itaconate). The presence and position of $-CH_3$ in aromatic ring influence the initial rates of polymerization and solubility in organic solvents. Polymers based on diesters of itaconic acid have received particular attention in recent years by Yazdani(36). Diesters of itaconic acid were polymerized by both bulk and emulsion techniques to produce a series of samples with ester chain length ranging from methyl to hexyl.

Shaabam et al(37-40) studied the copolymerization reaction of di-(tri-n-butyltin) itaconate with methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-chloroethyl acrylate, methyl methacrylate, allyl methacrylate, acrylonitrile, styrene and N-vinyl-2-pyrrolidinone. The copolymer composition of each sample was calculated from tin analysis. The monomer reactivity ratios for the systems studied were determined according to the Fineman-Ross and Kelen-Tüdős methods. They also studied the ternary copolymerization of di-(tri-n-butyltin) itaconate with acrylic acid esters, styrene and acrylonitrile. The experimental result for the azeotropic terpolymer composition were in good agreement with the theoretical values.

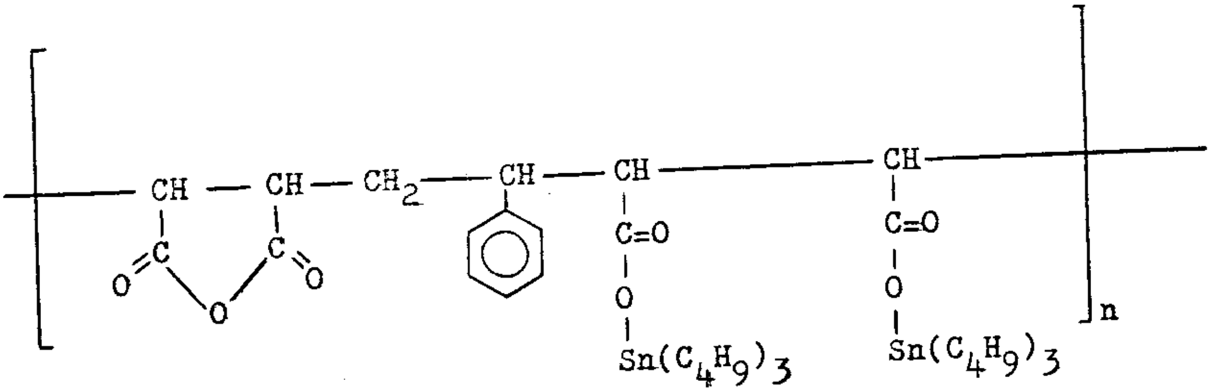
Ham and Ringwold(41) showed that vinyl benzoate polymers and copolymers were invariably crosslinked gels, and they attributed this to the monomer being bifunctional, in that radicals could add to the benzene ring as well as initiate normal polymerization through the vinyl group. The slow rate of polymerization of vinyl benzoate was noted that no explanation presented. The highly branched and cross-linked structure of vinyl benzoate was also shown by Smets and Hertoghe(42), who hydrolyzed the polymer and observed the drop in molecular weight which accompanied hydrolysis. This behaviour is consistent with Ham and Ringwald's picture of branching through addition to the aromatic nuclei such links would be readily hydrolyzable. Burnett and Wright(43) showed that the rate of polymerizayion was first order with respect to catalyst concentration or to the light intensity in case of photoinitiated polymerizations. The monomer t-butyl-p-vinylperbenzoate (TBVP) was prepared by Dalton and Tidwell(44), and was homo-and copolymerized with styrene, methacrylonitrile, isoprene and phenylmethacrylate.

Ready et al.(45) studied the free radical copolymerization of N-vinyl-2-pyrrolidone with 2,4,5-trichlorophenyl acrylate in chloroform, and in the presence of AIBN, at 50 °C.

Rohan et al.(46) prepared o-methacryloyloxybenzoic acid by the reaction of salicylic acid with methacryloylchloride using potassium carbonate as catalyst and acetone as solvent in the presence of a little amount of hydroquinone. The polymerization of o-methacryloyloxybenzoic acid deviates from the classic free radical polymerization mechanism when the reaction is carried out in solution at moderatory high temperature. The mechanism is characterized by two reactions in the propagation step, the addition of monomers unit to polymeric chain and the formation of anhydride groups in the macromolecule chains as follows :

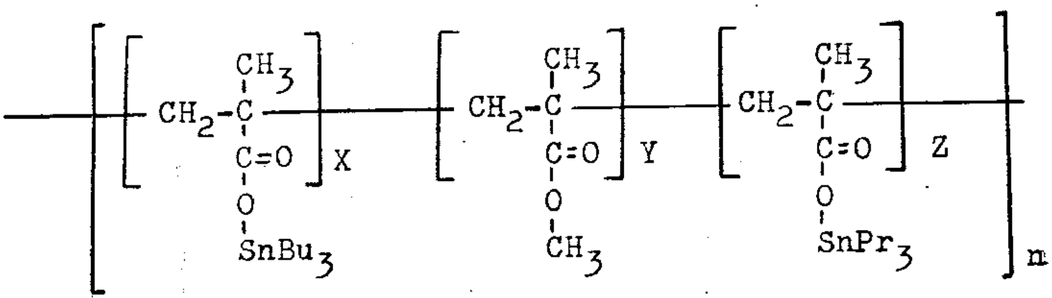


The copolymers of p-triphenyltin styrene and styrene or vinyl toluene, were prepared and studied kinetically by Sandler et al(47), who reported that the rate of addition of p-triphenyltin styrene monomer to its own radical is greater than the addition of styrene or vinyl toluene monomers suggesting that small blocks of the tin monomer unit should be present in the polymer network. Kochkin(48) and Rzaev(49) studied a series of co- and terpolymers prepared from the reaction of maleic anhydride, styrene and organotin diester of maleic anhydride, with the following general structure.



These polymers were found to be resistant to ultraviolt aging and have bactericidol and general antimicrobial behaviour .

Montemarano and Dyckman(50) reported that the incorporation of such biocidal compounds in polymeric backbones, such as polymethacrylates, polystyrenes and polyesters, produced long lived, low-leaching organotin polymers. This chemical conservation of the organotin toxin will provide longer-term biocidal effect, while reducing the pollution hazard attributed to presently used toxic compounds. These organotin polymers were found to be transparent, nonwettable, film-forming and effective against bacteria, algae and fouling organisms. They also prepared organotin polymethacrylates based on tributyltin methacrylate with the following structure :



Zabotin and Malysheva(51) studied the copolymerization of tributyltin acrylate with alkyl acrylate in solution and reported that the reactivity ratios of alkyl acrylate with tributyltin acrylate decreased with increasing length of the alkyl chain. The monomer reactivity ratios of tributyltin methacrylate with glycidyl methacrylate were determined by Subramanian et al(52) who reported that the copolymer produced could be self-cured to a crosslinked product by heating.

The monomer reactivity ratios for the copolymerization reactions of tri-n-butyltin acrylate or methacrylate, n-propyl methacrylate, n-butyl methacrylate, allyl methacrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, acrylonitrile and styrene were investigated(53-56). r_1r_2 values obtained indicate that most of the studied copolymer systems should have random distribution of the monomer units in the copolymer chain and the tendency towards alternation increases with increasing the alkyl chain length of the methacrylate or acrylic acid ester used.

Messiha(57) investigated the binary and ternary copolymerization reaction of tri-n-butyltin acrylate and methacrylate with vinyl acetate and N-vinyl pyrrolidone. The monomer reactivity ratios obtained for the organotin monomers were much greater than the corresponding values of vinyl acetate and n-vinyl pyrrolidone. Ikladious and Shaaban(58) determined the monomer reactivity ratios for the copolymerization reactions of tri-n-butyltin meleate with methyl methacrylate,