INTRODUCTION

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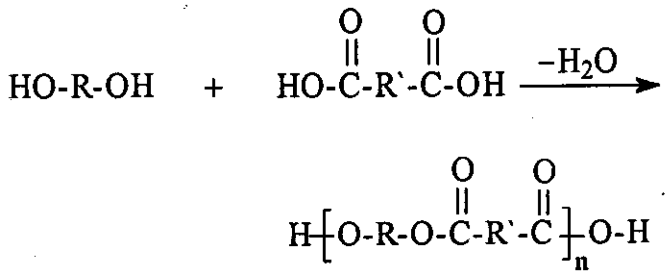
1.1 Homopolymerisation of Monomers:

1.1.1 Introduction:

Polymers are macromolecules generated by joining together a large number of smaller molecular units (monomers). The overall reaction which combines these monomers is called polymerization(1). The classification used in the formative years of polymer science was due to Carothers and is based upon comparison of the molecular formula of a polymer with that of the monomer(s) from which it was formed. Condensation polymers are those which have repeating units with fewer atoms than were present in the monomers from which they were formed. This usually arises from chemical reactions which involve the elimination of a small molecule(2).

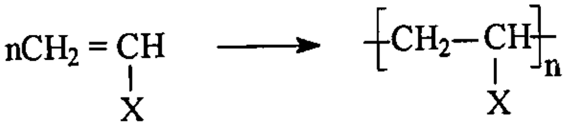
The reaction time in the preparation of condensation polymers generally affects the molecular weights of the generated polymers. The polymer molecular weight rises steadily during the reaction. For example a polyester is formed by typical condensation reactions between bifunctional monomers, with elimination of water in equation (1).



$$\text{HO-R-OH} \quad + \quad \text{HO-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R}'\text{-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OH} \xrightarrow{-H_2O}$$

$$\text{H}\left[\text{O-R-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R}'\text{-}\overset{\overset{\text{O}}{\|}}{\text{C}}\right]_n\text{O-H} \qquad (1)$$

Addition polymers are those which have repeating units with identical molecular formula to those of the monomers from which they are formed(2). Polymers formed from the polymerization of vinyl monomers are the most common in this class as shown in equation (2).



$$n\mathrm{CH_2}=\underset{\mathrm{X}}{\underset{|}{\mathrm{CH}}} \longrightarrow \left[\mathrm{CH_2}-\underset{\mathrm{X}}{\underset{|}{\mathrm{CH}}}\right]_n \qquad (2)$$

The reaction time in the preparation of addition polymers affects the number of polymer molecules, while it generally has little or no effect on the molecular weights of the general polymers. Such polymers can have high average molecular weight at all percentages of conversion. The reaction mixture contains monomer and high molecular weight polymer with the monomer concentration decreasing with reaction time(1).

The method of classification according to Carothers was found to be unsatisfactory when it was recognised that certain condensation polymers may be produced by methods typically used to prepare addition polymers(2). A better basis for classification is provided by considering the underlying polymerisation mechanisms, of which there are two general types. Polymerisations in which the polymer chains grow step-wise by reactions that can occur between any two molecular species are known as step-growth polymerisations. Polymerisations in which a polymer chain grows only by reaction of monomer with a reactive end-group on the growing chain are known as chain-growth polymerisations, and usually require an initial reaction between the monomer and an initiator to start the growth of the chain.

Step polymerisation can be defined as follows:

Linear step polymerisation involves reactions of bifunctional monomers. Polycondensation involves reactions in which small molecules are eliminated, with for example the formation of linear polyester as mentioned before. If a trifunctional monomer was included, reaction at each of the three functional groups would lead initially to the formation of a branched polymer.

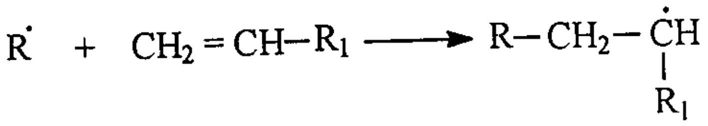
Chain polymerisation can be classified as follows:

a- Free radical polymerisation.
b- Ionic polymerisation includes cationic and anionic polymerisation.

The research in this thesis is concerned with chain polymerisation, and specially with propagation of free radicals.

1.1.2. Free Radical Chain Polymerisation:

A free radical(4,5) is a molecular or an atomic reactive intermediate in which the normal bonding system has been modified such that each of the intermediates possess an unpaired electron(6,7) as in equation (3).

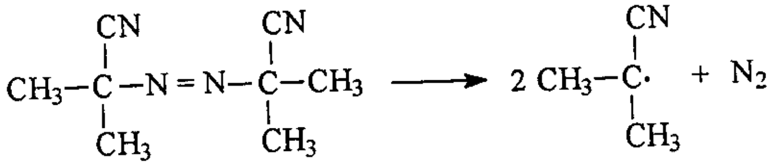


$$R^{\bullet} + CH_2=CH-R_1 \longrightarrow R-CH_2-\underset{\displaystyle R_1}{\overset{\bullet}{C}H} \qquad (3)$$

Polymerization solvents include tetrahydrofuran, dioxane, toluene, and N, N-dimethylforamide (DMF). In this thesis DMF was used as solvent due to the high solubility of acrylamide-and acryloyloxy-derivatives and the resulting polymers in this solvent. The polymerization process can be divided into 3 stages:

a- Initiation:

Free radicals are generated by a variety of thermal, photochemical and redox methods(1,6). In order to function as a useful source of radicals, an initiator system should be readily available, stable under ambient or refrigerated conditions and possess a practical rate of radical generation at moderate temperatures (< 150 °C). The initiator system used in this research was 2,2′-azobisiobutyronitrils (AIBN) which produced free radicals through thermal decomposition. A driving force for this decomposition is the production of stable nitrogen gas(7) in equation (4).

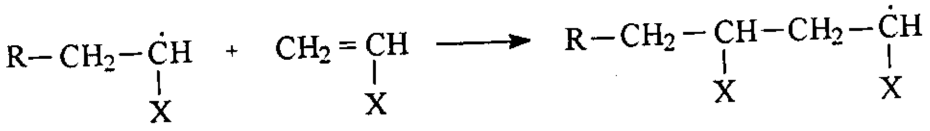


$$CH_3-\underset{CH_3}{\overset{CN}{C}}-N=N-\underset{CH_3}{\overset{CN}{C}}-CH_3 \longrightarrow 2\,CH_3-\underset{CH_3}{\overset{CN}{C}}\cdot + N_2 \qquad (4)$$

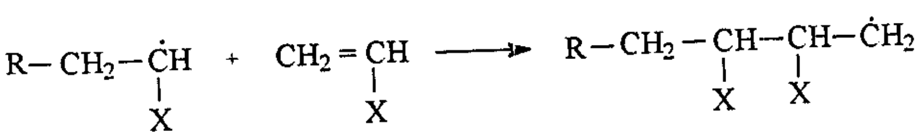
b- Propagation (Chain Growth):

This reaction involves the addition of a free radical to the double bond of a monomer molecule. The product must itself be a free radical and the process is then repeated(7). There are three forms of monomer addition, namely: head to tail, head to head and tail to tail, the most likely form being head to tail.

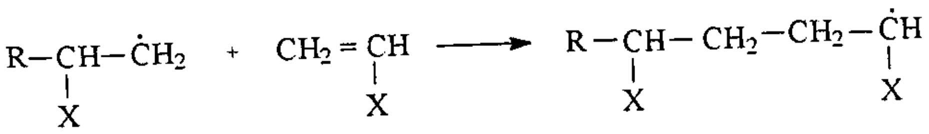
The principal reason for head to tail addition, equation (5), is the greater thermodynamic stability of a free radical, which can be explained by two factors: (i) a steric effect, as monomers used in addition polymerisation reactions are generally substituted at the head side with bulky groups (X) that hinder addition to another monomeric head as illustrated in equation (6), (consequently, a steric effect minimises head to head polymerisation) and (ii) a resonance effect, as substituents on a monomeric head are normally efficient radical stabilisers (electron withdrawing groups), and accordingly, a radical should be more stable at the head than at the unsubstituted tail, which also increases the chance of head to tail addition over tail to tail addition in equation (7).



$$\mathrm{R{-}CH_2{-}\underset{X}{\dot{C}H}} + \mathrm{CH_2{=}\underset{X}{CH}} \longrightarrow \mathrm{R{-}CH_2{-}\underset{X}{CH}{-}CH_2{-}\underset{X}{\dot{C}H}} \quad (5)$$



$$\mathrm{R{-}CH_2{-}\underset{X}{\dot{C}H}} + \mathrm{CH_2{=}\underset{X}{CH}} \longrightarrow \mathrm{R{-}CH_2{-}\underset{X}{CH}{-}\underset{X}{CH}{-}\dot{C}H_2} \quad (6)$$



$$\mathrm{R{-}\underset{X}{CH}{-}\dot{C}H_2} + \mathrm{CH_2{=}\underset{X}{CH}} \longrightarrow \mathrm{R{-}\underset{X}{CH}{-}CH_2{-}CH_2{-}\underset{X}{\dot{C}H}} \quad (7)$$

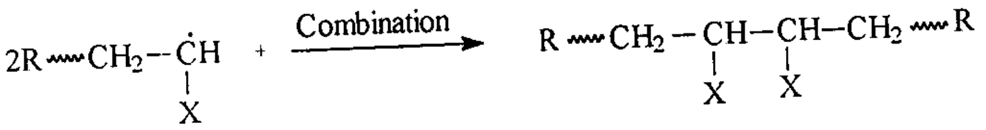
c-Termination:

Free radical chains can be terminated by:

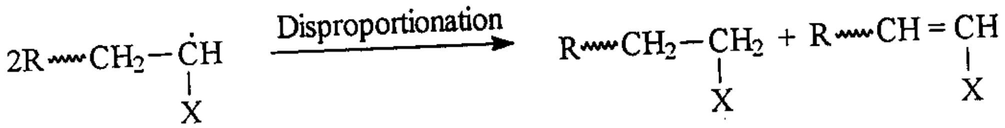
(i) Reaction of an active chain end with an initiator radical, such a reaction being defined as primary radical termination.

(ii) Interaction with impurities, e.g. oxygen, or inhibitors such as hydroquinone(5). Such reactions can retard or stop polymerization.

(iii) Termination may occur either by combination, where two radicals can simply combine together to form a long chain or disproportionation, where 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, as in equation (8,9). It should be noted that in combination termination of polymer with two initiator fragments (R) per polymer molecule is produced, but disproportionation produces polymer molecules with a single initiator end group. Free radical polymerizations often terminate predominantly by combination rather than disproportionation(1).



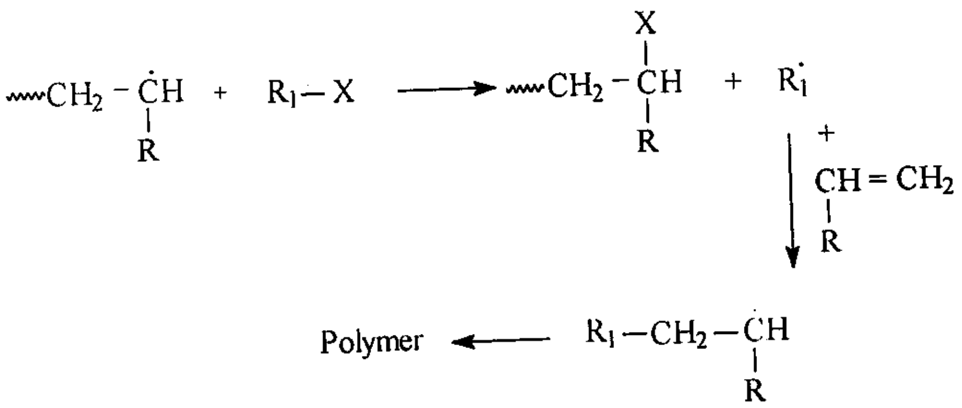
$$2R\sim CH_2-\underset{X}{\dot{C}H} + \xrightarrow{\text{Combination}} R\sim CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2\sim R \qquad (8)$$



$$2R\sim CH_2-\underset{X}{\dot{C}H} \xrightarrow{\text{Disproportionation}} R\sim CH_2-\underset{X}{CH_2} + R\sim CH=\underset{X}{CH} \qquad (9)$$

d-Chain transfer:

In an ideal free radical polymerization chains become initiated, they propagate, and they are then terminated. The deviation from ideality occurs when a propagating oligomer or polymer radical reacts with another molecule, not by addition, but by abstraction hydrogen or chlorine, for example, from another molecule and thus becomes saturated, and the molecule from which the atom has been abstracted will then become a radical and start a new chain(7). Then chain reaction therefore continues, even though the chain growth of the first macromolecule has stopped. It has transferred the growth reaction to another molecule. This reaction is therefore called a chain transfer reaction, as in equation (10).



$$\sim CH_2-\underset{R}{\dot{C}H} + R_1-X \longrightarrow \sim CH_2-\underset{R}{\overset{X}{CH}} + \dot{R_1} \xrightarrow{+\ \underset{R}{CH}=CH_2} R_1-CH_2-\underset{R}{\dot{C}H} \longrightarrow \text{Polymer} \qquad (10)$$

Chain transfer of this type may occur with initiator, monomer, or solvent. Shorter chain lengths result and hence, lower the number average molecular weight (M_n). Among the common initiators, hydroperoxides have a tendency to transfer reactions, whereas benzoyl peroxide, and especially AIBN, do not take part in transfer reactions.

1.1.4 Kinetics of Homopolymerization:

The three basic steps in the polymerization process can be analysed to obtain equations that describe the kinetics of free radical polymerisation.

Initiation is a two stage reaction. Decomposition of initiator I.

$$I \xrightarrow{K_d} 2R^{\bullet} \tag{11}$$

is followed by attack of radical *R* on a monomer *M* to form a chain carrier *RM*.

$$R^{\bullet} + M \xrightarrow{K_i} RM^{\bullet} \tag{12}$$

The rate of initiation R1 (thermal initiation) is then the rate of production of chain radicals.

$$R_i = \frac{d\,[RM^{\bullet}]}{Dt} = 2\,k_d f\,[I] \tag{13}$$

where *f* represents the efficiency of conversion of these radicals into propagating chains and K_d and K_I are rate constants. Propagation is the addition of monomer to the growing radical.

$$RM_n^{\bullet} + M \xrightarrow{K_p} RM_{n+1}^{\bullet} \tag{14}$$

where K_p is the rate constant for propagation. The rate of bimolecular propagation reaction is assumed to be the same for each addition.

$$R_p = K_p [M][M^\bullet] \quad (15)$$

Where $[M]$ represents the concentration of the propagating chains and $[M]$ is usually low at any particular time. Termination is also a bimolecular process depending on $[M]$. The rate of termination R_t is given by:

$$R_t = 2 K_t [M^\bullet][M^\bullet] \quad (16)$$

The rate constant K_t can be obtained from two possible mechanisms, combination or disproportionation. In the polymerization of many momomers by the thermal decomposition of radical initiators, the mechanism is usually by combination(5,8). A steady state is reached when the rate of radical formation is exactly counterbalanced by the rate of destruction.

$$R_i = R_t \quad (17)$$

For a polymerization involving the thermal decomposition of a radical initiator, it follows from equations (13) and (16) that

$$2 K_t [M^\bullet]^2 = 2 K_d f [I] \quad (18)$$

Therefore, the radical concentration is given by

$$[M^\bullet] = \{ K_d f [I] / K_t \}^{0.5} \quad (19)$$

Because the radical concentration is too small to be determined in conventional polymerization experiments, it is replaced in equation (15) by substitution of equation (19), giving

$$R_p = K_p \ \{f K_d \ [I] / K_t \ \}^{0.5} \ [M] \qquad (20)$$

Therefore, the rate of polymerization is proportional to the monomer concentration and to the square root of the initiator concentration, if f is high. For a low efficiency initiator, f becomes a function of [M], and the rate is proportional to $[M]^{(1,5)}$.

The kinetic chain length is a measure of the average number of monomer units reacting with an active centre and is given by

$$\bar{v} = \frac{R_p}{R_i} = K^2_p[M]^2 / 2 \, K_t \, R_p \qquad (21)$$

For termination by combination under steady state conditions, it follows that $\bar{v}$ is related to the average degree of polymerisation $\bar{X}_n$ by

$$\bar{X}_n = 2\bar{v} \qquad (22)$$

where $\bar{X}_n$ is given by

$$\bar{X}_n = \bar{M}_n / M_o \qquad (23)$$

where $\bar{M}_n$ is the number average molecular weight and $\bar{M}_o$ is the molecular weight of the monomer.

Therefore, the kinetic chain length is inversely proportional to the rate of polymerization. From an analysis of the temperature dependence of the rate of polymerization, it follows that the rate of polymerization will increase and the kinetic chain length will decrease on raising the temperature. The kinetic chain length is also inversely proportional to initiator concentration. Therefore, increasing the initiator concentration will decrease the kinetic chain length (i.e. molecular weight).

1.2 Copolymerization Reactions of Monomers:

1.2.1 Free radical copolymerization:

Free-radical copolymerization may be defined as a process whereby two or more monomers are integral parts of a high polymer via radical chain reaction. A copolymer is a product resulting from such a process. The importance of the free-radical copolymerization, it can be considered 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 be 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.

1.2.1.1 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 equations can be written for various types of addition possible(4&5)

$$-\!\sim\!\sim\!\sim M^{\cdot}_1 + M_1 \xrightarrow{K_{11}} \sim\!\sim\!\sim M_1M^{\cdot}_1 \quad \text{rate} = K_{11}\,[M_1]\,[M_1] \qquad (24)$$

$$-\!\sim\!\sim\!\sim M^{\cdot}_1 + M_2 \xrightarrow{K_{12}} \sim\!\sim\!\sim M_1M^{\cdot}_2 \quad \text{rate} = K_{12}\,[M^{\cdot}_1]\,[M_2] \qquad (25)$$

$$-\!\sim\!\sim\!\sim M^{\cdot}_2 + M_2 \xrightarrow{K_{22}} \sim\!\sim\!\sim M_2M^{\cdot}_2 \quad \text{rate} = K_{22}\,[M^{\cdot}_2]\,[M_2] \qquad (26)$$

$$-\!\sim\!\sim\!\sim M^{\cdot}_2 + M_1 \xrightarrow{K_{21}} \sim\!\sim\!\sim M_2M^{\cdot}_1 \quad \text{rate} = K_{21}\,[M^{\cdot}_2]\,[M_1] \qquad (27)$$

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, M_1 .... etc. If a steady sate is reached instantly after the polymerization is started, then the total concentration of $M^{\bullet}_1$ and $M^{\bullet}_2$ will remain constant, and the rate of conversion of $M^{\bullet}_1$ to $M^{\bullet}_2$ will equal the rate of conversion of $M^{\bullet}_2$ to $M^{\bullet}_1$:

$$K_{21}\,[M_2]\,[M_1] = K_{12}\,[M_1]\,[M_2]$$

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

$$- d\,M_1 / dt = K_{11}\,[M^{\bullet}_1]\,[M_1] + K_{21}\,[M^{\bullet}_2]\,[M_1] \qquad (28)$$

$$- d\,M_2 / dt = K_{12}\,[M^{\bullet}_1]\,[M_2] + K_{22}\,[M^{\bullet}_2]\,[M_2] \qquad (29)$$

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

$$\frac{d[M_1]}{d[M_2]} = \frac{K_{11}[M^{\bullet}_1][M_1]+K_{21}[M^{\bullet}_2][M_1]}{K_{12}[M^{\bullet}_1][M_2]+K_{22}[M_2][M^{\bullet}_2]} \qquad (30)$$

$$= \frac{[M_1]}{[M_2]}\left[\frac{K_{11}[M^{\bullet}_1]+K_{21}[M^{\bullet}_2]}{K_{12}[M^{\bullet}_1]+K_{22}[M^{\bullet}_{21}]}\right] \qquad (31)$$

Multiplying by

$$[M_2] / K_{21}\,[\,M_1]$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{\dfrac{K_{11}[M^{\bullet}_1][M_1]}{K_{21}[M^{\bullet}_2]}+[M_2]}{\dfrac{K_{12}[M^{\bullet}_1][M_2]}{K_{21}[M^{\bullet}_2]}+\dfrac{K_{22}}{K_{21}}[M_2]}\right)$$

since

$$[M_1] = \frac{K_{12}}{K_{21}}\,\frac{[M^{\bullet}_1][M_2]}{[M^{\bullet}_2]}\text{, then}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{M_2}\left(\frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]}\right) \qquad (32)$$

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

$$F_1 = \frac{r_1 f_2^2 + f_1 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}} \qquad (33)$$

where

F_1 = mole fraction of monomer M_1 in copolymer, and

f_1 = mole fraction of monomer M_1 in feed

1.2.2 Types of copolymerization behaviour :

From the copolymerization equation (14-17), if $K_{11} > K_{12}$ and $K_{22} > K_{21}$ copolymerization would be insignificant and a mixture of homopolymers or blocks of 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_1 r_2) is unity, less than unity, or greater than unity as follow:

a- When $r_1 r_2 = 1$, the two types of propagation species $M^{\bullet}_1$ and $M^{\bullet}_2$ show the same preference for adding one or the other of the two monomers, and the monomers unit will be incorporated in a random monomer influenced by the feed composition. Thus, substituting $r_2 = 1/r_1$ in equation (32) and (33) one get:

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \qquad (34)$$

and
$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2} \tag{35}$$

b- When $r_1 r_2 < 1$, 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 alternation 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 copoymer and the feed composition are the same, and the copolymerization occurs without change in the feed composition to give:

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \tag{36}$$

by substitution in equation (33) one gets:

$$F_1 = f_1 = \frac{1 - r_2}{2 - (r_1 + r_2)} \tag{37}$$

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 mixture of homopolymers.

1.2.3 Methods of calculating monomer reactivity ratios:

All methods for the determinations of monomer reactivity ratios involve the experimental determination of the copolymer composition formed from several different feed compositions. The techniques used for quantitative determination of copolymer composition include elemental analysis, radioisotopic labeling and ultraviolet, infrared and nuclear magnetic spectroscopy methods. All procedures depend on copolymerizations carried out to low degrees of conversion 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(9), describes the development of theoretical basis for comparing the behaviour of monomers in copolymerization for addition polymerization, and the application of the general concept to the copolymerization of styrene and methyl methacrylate by a free radical mechanism.

This method depends on the copolymerisation equation (32), which can be expressed in terms of molar ratios instead of concentrations as:

$$b = \frac{r_1 a + 1}{r_2 / a + 1} \qquad (38)$$

where $a = [M_1] / [M_2] = f_1 / (1-f_1)$ and $b = d[M_1] / d[M_2] = F_1/(1-F_1)$. Data for the feed and copolymer compositions for each experiment with a given feed are substituted into equation (38) and r_2 is plotted as a function of various assumed values of r_1. Each experiment yields a straight line and the intersection of the lines for different feeds gives the best values of r_1 and r_2. Any variations observed in the points of intersection of various lines are a measure of the experimental errors in the composition data and the limitations of the mathematical treatment. The composition data can also be treated by linear least-squares regression analysis instead of the graphical analysis.

The disadvantages of this method include:

1- The reproducibility of the result and the size of the triangular intersection obtained in an experiment depend on both the procedure for isolating the polymer and the precision of the carbon analysis.

2- Extensive calculations are required, and only a qualitative measure of the precision of the estimates r_1 and r_2 is provided.

3- The observer is required to subjectively weight the data, a task not consistently done even by the same observer.

b- Fineman-Ross method

The method of Fineman and Ross$^{(10)}$ represents a considerable improvement in the direction of straightforward analysis of copolymerization data. It involves carrying out the copolymerizations to low conversions and using the approximate form of equation (33). The ratios r_1 and r_2 may then be obtained graphically from the initial and final slopes of the usual copolymerisation curve in which the polymer composition is plotted against the monomer composition. By defining $a = [M_1] / [M_2] = f_1/(1-f_1)$ and $b=d[M_1]/d[M_2] = F_1/(1-F_1)$ then, the equation can be rearranged to

$$a-\frac{a}{b}=r_1\frac{a^2}{b}-r_2 \qquad (39)$$

Therefore, a plot a-(a/b) as ordinate and a^2/b as abscissa is a straight line whose slope is r_1 and whose intercept is minus r_2. The disadvantages of this method include:

1- Large uncertainties in the slopes, and consequently in the r_1 and r_2 values, may occur, particularly in those cases where the slopes are steep or where experimental data at very low and very high concentration ratios are unavailable.

2- The reliability of the determined values can be increased by a tedious method of calculating theoretical curves for pairs of values of r_1 and r_2 and fitting them to the experimental curves.

Tidwell-Mortimer method:

Tidwell and Mortimer$^{(11)}$ pointed out that reactivity ratios should be determined by a non-linear regression technique and that the error associated with the estimates of r_1 and r_2 was a joint error which should be expressed as a joint confidence region. Many reactivity ratios are determined by a set of experiments where the monomer feed ratios are varied. However, Tidwell and Mortimer(12) used a different approach based on the statistical design of experiments using the instantaneous copolymer composition equation and a non-linear least squares estimation. They recommended an experimental design which involved doing a number of experiments at two compositions of monomer only defined by:

$$F_a = \frac{2}{2 + r_1} \qquad (40)$$

and

$$F_b = \frac{r_2}{2 + r_2} \qquad (41)$$

where F_a and F_b are the comonomer feed ratios. The r_1 and r_2 values used to define these feed compositions were estimates based on preliminary experiments and chemical intuition. However, this method requires tedious computerised procedures.

d-Kelen-Tüdős method:

This method proposed by Kelen and Tudos(13) for calculating the monomer reactivity ratios is based on a new graphically linear equation as follows:

$$\eta = (r_1 + r_2 / \alpha)\,\xi - (r_2 / \alpha) \qquad (42)$$

where

$$\eta = \frac{a(b-1)}{\alpha b + a^2}, \quad \xi = \frac{a^2}{\alpha b + a^2} \text{ and } \alpha = \frac{a_{min} \times a_{max}}{(b_{min} \times b_{max})^{\frac{1}{2}}}$$

where $a = [M_1] / [M_2] = f_1 / (1-f_1)$ and $b = d[M_1] / d[M_2] = F_1 / (1- F_1)$

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

Advantages

1- An arbitrary positive constant α is introduced to spread the data more evenly so as to give equal weighting to all data points.

2- Re-indexing of the monomers and reactivity ratios does not change the calculated results.

3- The method allows visual estimation of the fact whether the copolymer composition equation (32) is adequate for the experimental data in a given system.

4- The linearity of the plot made with equation (42) may be used as a test for the assumptions required in the derivation of equation (32) for copolymer composition(14). Examples of curved plots according to equation (42) have been identified for cationic copolymerization systems so that the approximations implicit in the conventional copolymer composition equation do not hold(15).

d- Jashi-Kapur method(16)

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. But the locating of the best intersection from the "probable area" confined by different straight lies on the r_1, r_2 plot. The coordinates of the point of intersection (r_1r_2) and the tangent value of the angle of intersection (tan θ) are calculated. From the following two equation of the intersecting lines given by the general copolymer composition (for how conversion) equation (29).

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

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

therefor:

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

and

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

where

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

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

e-Yezrilev, Brokhina-Roskin method:

Yezilev, Borkhina and Roslein(17) transformed the linear equation of copolymer composition into symmetrical form as

$$a/b^{1/2}.\ r_1 - b^{1/2}/a.\ r_2 + (1/b^{1/2} - b^{1/2}) = o$$

where

a $= M_1 / M_2$ (molar ratios of the two monomers in the commoner mixtures)

and $b = \frac{m_1}{m_2}$ (molar ratios of the two monomers in the copolymer). In thus 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.

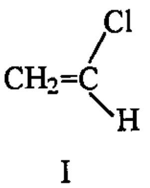
IV- Factors affecting the monomer reactivity:

a-Resonance Effects:

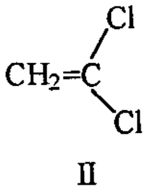
The reactivity of monomers depends on the resonance stabilitsation of the radical produced from the monomer. Delocalisation of π-electrons improves resonance stabilisation(1). The order of substituents in enhancing radical reactivity is opposite to that for monomer reactivity. A substituent which increases monomer reactivity does so because it stabilises and decreases the reactivity of the corresponding radical.

b-Steric Effects:

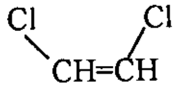
The rates of radical-monomer reactions are also dependent on steric hindrance. For example, compared to vinyl chloride (I), the reactivity of vinylidene chloride (II) increases, whereas the reactivity of 1,2-dichloroethene (III) decreases(1). The former effect is due to increased stabilistation of the resulting radicals due to two Cl subsituents, whereas the latter effect is a result of steric hindrance between the monomer and the radical to which it is adding.



I



II



III

A comparison of *cis*- and *trans*-1,2-dichloroethene shows the trans isomer to be the more reactive. The difference in reactivity has been attributed to the inability of the cis isomer to achieve a completely coplanar conformation in the transition state.

c-Alternation (Polar Effect):

The significant conclusion is that the tendency toward alternation increases as the difference in polarity between the two monomers increases. Monomers with electron donating and electron withdrawing substituents have widely differing polarities and, when copolymerised with each other, can produce highly alternating copolymers(18). The addition of a Lewis acid, such as trialhyaluminum, can increase the tendency to form alternating copolymers, even between monomers which don't normally copolymerise in an alternating fashion(19,20).

d-Solvent effect:

Free radical copolymerization are generally carried out in solution. Copolymerisation involving non-polar monomers with monomers containing ionisable groups, groups capable of hydrogen bonding interactions or even polar groups may show a marked influence depending on the nature of the solvent(21) this will give rise to change in measured reactivity ratios varying with solvent Harwood(22) found that, although the reactivity ratios may vary considerably as the reaction solvent is changed, copolymers with identical compositions had the same microstructure. Harwood proposed that the partitioning of monomers between solvent and growing radicals was important. The reactivity ratios determined for polar monomers were products of the ture reactivity ratios and the partition coefficients. The reactivity ratios are therefore independent of solvent but the solvent will influence the relative local concentrations of the comonomers to growing chain end.

V-Monomer reactivity and interpretation Q-e scheme:

The monomer reactivity ratio values, r_1 and r_2; describe the relative tendency of two monomer to add to a particular growing chain(2). The reactive end of the growing chain is a free radical derived from are 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 relation was proposed to be

$$r_1 = \frac{K_{11}}{K_{12}} = \left(\frac{Q_1}{Q_2}\right)[\exp - e_1(e_1 - e_2)\ ] \qquad (43)$$

$$r_2 = \frac{K_{22}}{K_{21}} = \left(\frac{Q_2}{Q_1}\right)[\exp - e_2(e_2 - e_1)\ ] \qquad (44)$$

$$r_1 r_2 = \exp. - (e_1 - e_2)^2 \qquad (45)$$

$$\ln r_1 r_2 = - (e_1 - e_2)^2 \qquad (46)$$

Price choose stryrene as the standard monomer with the value Q=1 e = 0.8. The Q and e value 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 predicated behaviour is not always exactly like the experimental result the Alfry-Price scheme never the less leads at least to good approximation. The major shortcoming of

Q – e scheme is that all radical polymerization involve not only resonance and polar factors, but also steric factors. It is certainly conceded that steric limit the applicability of the scheme 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(23,24) and general expressions for value of the monomer reactivity ratios by Alfrey and Gold finger(16), 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:

$$P_{11} = \left(1 + {}^{m_2}\!/_{r_1 m_1}\right)^{-1} \tag{47}$$

$$F_{111} = P_{11}^{\ 2} \tag{48}$$

$$P_{12} = \left(1 + {}^{r_1 m_1}\!/_{m_1}\right)^{-1} \tag{49}$$

$$F_{212} = P_{12}^{\ 2} \tag{50}$$

$$F_{112} = 2\,P_{12}\,(1 - P_{12}) \tag{51}$$

$$P_{22} = \left(1 + {}^{m_1}\!/_{r_2 m_1}\right)^{-1} \tag{52}$$

$$F_{222} = P_{22}^{\ 2} \tag{53}$$

$$P_{21} = \left(1 + \frac{r_2 m_2}{m_1}\right)^{-1} \qquad (54)$$

$$F_{121} = P_{21}^{\ 2} \qquad (55)$$

$$F_{221} = 2\,P_{21}\,(1 - P_{21}) \qquad (56)$$

The sequence distributions of the monomer units a long the copolymer chains where calculated from the monomer reactivity ratio basis of terminal copolymerization model(25). The variation in sequence distribution of the triad are represents as f_{111}, f_{212}, f_{112}, f_{121} and f_{221}.

5-Mode of action of organotins:

It may be stated that only very few organotin compounds e.g. triethyltin salts are highly toxic and economically important tributyl-, dibutyl- and triphenyltin compounds are known which are hardly toxic at all.

The main site of action of these compounds appears to be in the central nervous system(26). The biochemical action of the trialkytin compounds is their interference with oxidative phosphorylation, while the dialkyltin compounds act in a manner similar to arsenals, i.e they inhibit α-keto acid oxidases, which contain dithiol groups. Monoalkyltin compounds show range a low degree of toxicity.

The success of organotin polymer can be summarized by(27).

1- Organotin polymer are proven effective antifouling agents.

2- Chemically binding the toxic organotin moiety in the organotin polymer provides a low leading rate, thus offering a longer service life and negligible environmental impact.

3- Optimum antifouling performance of organotin polymers by modifying the polymer matrix.

4- Incorporation of two or more different types of organotin moieties widens the killing spectrum of the organotin polymers.

5- Organotin polymers may be synthesized with air pollution exempt solvent's.

Factors which influence the rate of hydrolysis of organotin polymers include polymer type, degree of cross-linking within the polymer backbone, the degree of substitution by organotin group along the polymer backbone, and sea water temperature, salinity, oxygen content, hydrogen ion concentration and turbulence.

The exact mechanism by which the triorganotins exert their leathal effect on marine organisms is still not clear. Castelli and Yeager(28), described the possible theories which might describe the actual mode of action of organotin polymers, which is probably a combination of the following:

1- The molecular weight of the majority of organotin polymers is small enough to permit solution of the intact toxic substituted polymer.

2- The body fluids of the animals in some way catalyze the hydrolysis of the ester linkage and produce a local high concentration of the antifouling which then is able to eliminate the fouling organism.

3- The marine environment is responsible for the slow hydrolysis of the linkage anchoring the pesticide and this would provide a slow but nearly constant out flow at pesticide from the surface.

4- The polymeric materials can be envisioned as tight sponges in which the "holes" are filled by chemically bound toxins and the outflow from the polymer is governed by the chemical hydrolysis of the polymer-pesticide bond, not simply the dissolution of the toxicant.

5- The toxic surface itself which prevents fouling by giving the fouling organisms a (bad – taste) when they attempt to settle on the surface.

2.1 Acrylamides and methacrylamides:

The acrylamide family of monomers is a highly versatile group of chemical intermediates, producing polymers and copolymers having a highly polar functional group attached to the backbone which have major uses. Linear poly (acrylamide) is a hard glassy solid, soluble in water and most aqueous solutions of electrolytes, but insoluble in all but the most polar organic solvents. By replacing one or both of the hydrogen atoms on the nitrogen atom by organic groups, products with increasing solubility in organic solvents and decreasing water solubility are obtained. Numerous copolymers of acrylamide and its derivatives have been prepared. Acrylamide polymers having ionic substituent groups are useful as polyelectrolytes(29).

Acrylamide monomers contain two functional groups, the double bond and the amide group. The reaction of the double bond is characteristic of an electron deficient bond. Nucleophilic reagents add readily to both acrylamide and methacrylamide. Acrylamide and related monomers have been polymerized by free radical and by ionic initiators. Free radical initiated systems in aqueous media are the most common for acrylamide and methacrylamide. Free radical polymerizations of N-substituted acrylamides proceed at much lower rates than for acrylamide(29).

The retarding effect of the N-alkyl substituent is primarily steric and has been ascribed to suppression of both the rate constant for propagation K_p and the rate constant for termination K_t by the alkyl group. N,N′-disubstituted methacrylamides are so hindered by steric effects and the polar effects of the substituents that they are not susceptible to polymerization(30,31). Poly (-N-methylacrylamide) and low molecular weight poly(-N,N-dimethylacrylamide) are soluble in water.

The copolymerisation of acrylamide and methacrylamide occurs readily with acrylates, methacrylates, and most styrene derivatives but acrylamide and methacrylamide do not copolymerise readily with vinyl halides. The amide group is electron withdrawing and activities the double bond. Increasing alkyl substitution on the nitrogen atom causes the reactivity of the amide radical to decrease and the polarity of the double bond to become less positive. Increasing the size of the alkyl substituent causes a small decrease in reactivity(34). The effects of an N-alkyl substituent on methacrylamide are similar to those on acrylamide(35).

2.2 Organotin polymers:

In the past 30-40 years a number of new polymers containing metals as an integral part of the repeating structure unit have been prepared and their properties studied. There is a current trend high mammalian toxicity and their relatively adverse effects on the environment.

Organotin compounds are eventually degraded in nature to give non-toxic inorganic tin residues(36,37). Organotin polymers may be classified as substances containing tin atoms, bound to carbon, in the main chain or pendant in side chains.

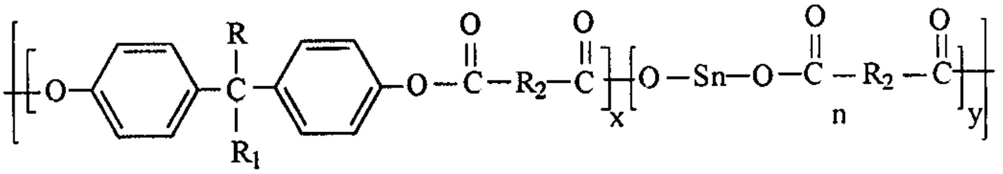
The actions of organotin compounds towards fungi, bacteria, and insects have been studied. The most important of these is the use of organotin compounds as fungicides in agriculture and applications in antifouling coatings and wood preservation(38).

2.2.1 Tin atoms in polymer main chain:

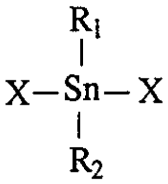
Generally, the synthesis of polymers containing tin atoms in the polymer backbone is carried out by condensation methods. For example, organotin polyesters were prepared directly by the reaction of organotin dihalides with the sodium salt of diacids as follows:

$$(R)_2SnCl_2 + R`(COONa)_2 \longrightarrow \left[Sn(R)_2OOCR / COO \right]_n + 2\,NaCl$$

Alternatively, dibutyltin diacetates or dibutyltin oxide can be reactes with diacides to form similar products(39), which were characterized by a lower degree of polymerization due in part to cyclisation reactions. Also, the condensation products of a bisphenol and a mixture of a diorganotin dihalide and acryl halide of a dicarboxylic acid were reported(40) to be linear chains as follows:

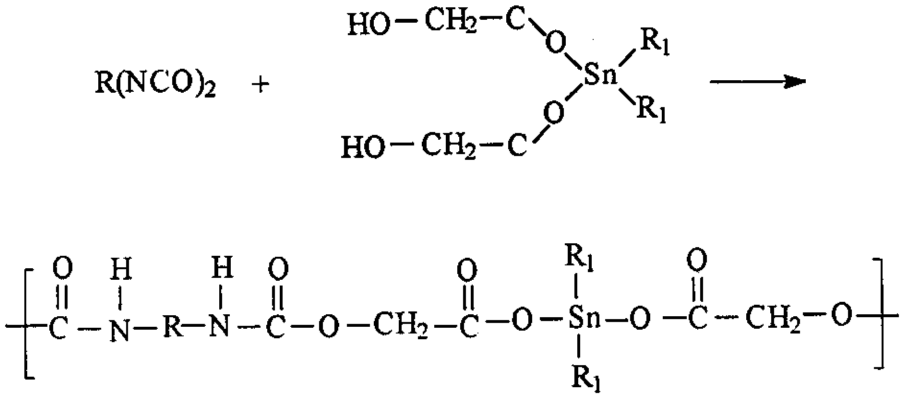


The diorganotin compound used in preparing the composition of this mixture may be represented by the formula:

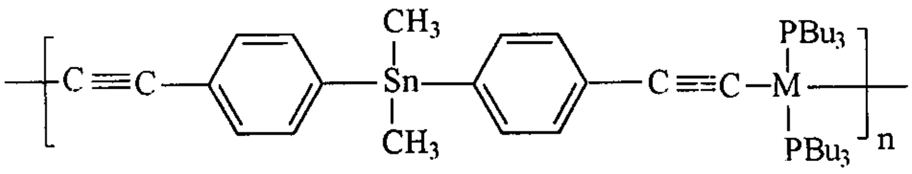


$$X-\overset{\displaystyle R_1}{\underset{\displaystyle R_2}{Sn}}-X$$

Where R_1 represents alkyl and aryl groups, and x represent halogen. A route to the synthesis of a polyurethane having tin in the polymer backbone has been described by Leebrick(41) who prepared polyurethanes containing tin as follows:



Organometallic polymers containing tin and transition metals in the main chain have been synthesised and characterized $^{(42,43)}$. The polymers in which tin and transition metals are regularly linked by a conjugated system through M-C bonds are as follows:



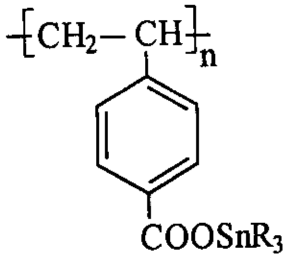
M = Pt or Pd

2.2.2 Tin atoms pendant to polymer chain:

Polymers containing organotin groups pendant to a carbon backbone are generally obtained by free radical initiated polymerisation of monomers through the reaction of organotin oxides or hydroxides with unsaturated acids as follows:

$$(R_3Sn)_2O + 2R' - CH = CR'' - COOH \longrightarrow 2\,R' - CH = CR'' - COOSnR_3 + H_2O$$

Where R, R`, R`` = H, alkyl or aryl. These unsaturated organotin monomers could also be prepared by the reaction of organotin halides or tetra-aryltins with an unsaturated organic acid. considerable numbers of organotin polyacrylates have been prepared from their respective monomers, which have been polymerized using bulk, solution and emulsion polymerisations; they may find applications as films, and coatings. Leebrick(45,46,47) prepared an analogous series of polymers based upon vinyl benzoic acid as illustrated below:



Atherton and co-workers(48,49) examined copolymers prepared from TBTMA (tri-butyltinmethacrylate) with MMA (methylmethacrylate), ST (styrene) and BA (butylacrylate), for the rate of toxin release and film erosion, and concluded that better control of toxin release is possible by the correct choice of the copolymer constituents. Not much work has been reported on studies of the kinetics and copolymerization parameters of organotin monomers to illustrate the composition and distribution of the organotin moiety within the copolymer chains. However, in a comparison study Koton(50,51) noted that triphenyltin methacrylate (TPTMA) polymerises more rapidly than MMA. Copolymers of *p*-TPHTST and ST, or vinyl toluene, were prepared and studied kinetically by Sandler et al(52) who reported that the rate of addition of *p*-TPHTST monomer to its own radical is greater than the addition of ST or vinyl toluene monomers suggesting that small blocks of the tin monomer units should be present in the polymer chain of the network.

The monomer reactivity ratios of TBTMA with glycidyl methacrylate were determined by Subramanian et al(53) who reported that the copolymer produced could be self-cured to a crosslinked product by heating. Garg et al studied the copolymerisation reaction of tri-n-butyltin acrylate (TBTA) and TBTMA with vinyl monomers containing either epoxy or hydroxy functional groups.

The monomer reactivity ratios for the copolymerisation reactions of TBTA or TBTMA with each of MMA, n-propyl methacrylate (PMA), EA, n-butylmethacrylate (BMA), allyl methacrylate (AMA), MA, BA, acrylonitrile (AN) and ST were studied(54,55,56). The values of r_1r_2 obtained indicated that most of the studied copolymer systems should have statistical distributions of the monomer units in the copolymer chain and the tendency towards alternation increases with increasing alkyl chain length of the methacrylate or acrylic acid esters used.

Dharia et al.(57) studied binary copolymerisation reactions of TBTMA with cyclohexylmethacrylate (CHMA), ethoxyethylmethacrylate (HEMA), ethylmethacrylate (EMA), 2-hydroxyethylmethacrylate (HEMA), and 2-hydroxypropylmethacrylate (HPMA). They found that TBTM-HPMA copolymers contained a greater proportion of HPMA than the feed. This phenomenon is more prononunced for TBTMA-HEMA copolymers. They concluded that steric effects may influence the reactivates of the different monomers towards the TBTMA polymer radical.

Diab et al.(58) investigated radical homopolymerizations and copolymerizations of 3-tri-n-butyltin styrene (3-BTST) with ST, EA, MMA, VA and AN. Monomer reactivity ratios and Q-e values were calculated.

Ready et al.(59) studied the free radical copolymerisation of NVP with *o*, *m*, *p*-trichlorophenyl acrylate in chloroform and in the presence of AIBN, at 50°C.

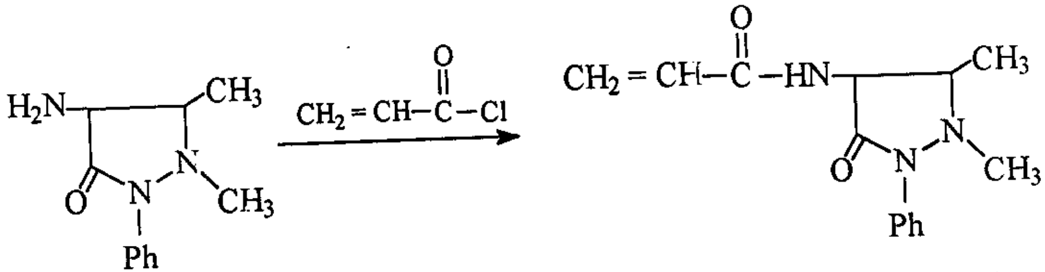
Endo et al.(60) synthesised a new organotin monomers, N-tri-n-butyltin propyl methacrylamide, and polymerised and copolymerised it with ST. They studied the application of a copolymer as catalyst for reductive dehalogenation of alkyl halides.

Moriya et al.(61) synthesised organotin polymers having both organotin and carbonate groups by the reaction of tri-n-butyltin hydride with monomers such as diallycarbonate and diethylene glycol bis (allyl carbonate) via hydrostannation.

Shaaban et al.(62) synthesised *p*-acryloyloxytri-n-butyltin benzoate (*p*-AOBTB) which was copolymerised with some acrylic monomers. The values of the monomer reactivity ratio of the organotin monomer. The values of the monomer reactivity ratio of the organotin monomer (r_1) for all copolymerisation reactions studied were nearly equal to zero, which indicates that, the growing radical ending with an organotin unit prefers an acrylic monomer rather than anorganotin monomer in the propagation stage. Azab(63) studied the thermal behaviour of *p*-AOTBTB-AN copolymers. The prepared homopolymer and copolymer were characterised by a variety of spectroscopic and thermal methods.

Joshi and Gupta(64) synthesised α-methyl *p*-acryloyloxytri-n-butyltin benzoate, which was homopolymerised in two solvents. Tawfik et al.(65) studied the effect of substitution on the reactivity of some *p*-phenylacrylamide derivatives with organotin monomers. They found that the *p*-acrylamidotoluene and *p*-acrylamidochlorobenzene polymerise slowly; on the other hand the *p*-acrylamido notrobenzene did not polymerise. This finding is in agreement with the fact that aromatic nitro compounds inhibit or retard the polymerisation of vinyl compounds. The copolymerisation parameters r_1 and r_2 have values indicating that the copolymer of *p*-acrylamidochlorobenzene with tri-n-butyltin acrylate shows a higher content of *p*-acrylamidochlorobenzene monomer. On the other hand, a *p*-acrylamido toluene-tri-n-butyltin acrylate copolymer shows a lower content of *p*-acrylamodotoluene. In contrast, the content of *p*-acrylamodo toluene monomer is much higher than that of tri-n-butyltin methacrylate monomer.

El-Hamouly et al.(66) studied the binary copolymerisation of N-antipyryl acrylamide (NAA) with MMA, BMA, AN and VA.



4-Amino antipyrine

N-Antipyryl acrylamide (NAA)

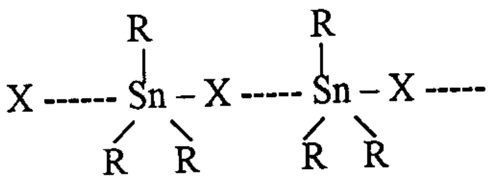
Samui et al(67) studied the antifouling paints compositions using copoly (MMA - MA)-Cu complex as a pigment critical pigment volume concentration (CPVC) was found to be around 35% pigment loading complex-based paints exhibits slower and steader leaching compared to Cu. At identical concentration of copper; the former effective leaching for a longer duration the leaching rate increases with pigment (copper complex) loading. Leaching in sea shows a small dip at the initial phase followed by rapid increase.

Valle et al[^(68)] studied a new antifouling paints that are more compatible with living species they studied specific acrylic polymers with a variable hydrophilic / hydrophilic balance. To evaluate the ability of these materials for hydrolysis, biocides release, and erosion, test panels with formulated films were prepared and immersed in sea water and to under stand the influence of the resin chemical structure on the paints antifouling efficiency. The degradation of these binders was reveated by the appearance of a product resulting from hydrolysis.

Anandrgo et al. (69) prepared controled release of sodium alginate (Na- Alg). The scanning electron microscopic studies indicated nonproms smoth surfaces and the differential scanning calorimetric data indicated the molecular level dispersion of the drug in the beads.

Masso et al. (70) prepared a copolymers of hydroxyethyl acrylate with glycidyl methocrylate (HA-GMA) by free radical polymerization the prepared copolymers could be used as disk shape.

Mohmoud et al(71) studied the copolymerisation parameters of p-AOTBTB with allyl methacrylate (AMA), NVP and VA. The monomer reactivity ratios indicate that the copolymerisations should give copolymers with a strong tendency to alternation. Associative organotin polymers were prepared, for example trialkyltin halide, as in the solid state organotin halide and pseudohalide have a strong tendency for intermolecular association. Tri-methyltin flouride(72) has been shown by X-ray crystallography to exist as polymeric species having the following structure:



Kjaer[73] investigated that the antifaling coatings containing a mixture of cuprous oxide and triorganotin compounds in combination with sophisticated release mechanisms are considered most efficient systems ever since the first biologically active materials were introduced into antifauling coatings.

Lanz[74] showed that the tributyl tin (TBT) leaching from all vessels coated with TBT-containing self-polishing copolymer coating has caused damage to marine organisms living close to the shipping lanes. Despite the portent of further restrictions on tin-based antifoulings. Manufactures of coatings containing organotin that such antifoulings which last five years for vessels on ocean passages is not only in the ship operators best interest. In addition to reduced fuel consumption and lower exhaust emission, the advantage of langer dry-docking intervals will mean less pollution caused hull painting operations.

Kenway[75] synthesis polymeric herbicide system based on a phosphorus-nitrogen containing polymer was carried-aut by melt poly condensation of phenyl phosphoric dichloride with N-(2,4-dichloro-phenoxy acetyl) diethanolamine (2-,4-D diolamide). The release of 2,4-D from the polymer was investigated.

The preparation(76) and structural characterization of polymeric herbicide consisting of 2,4-D and 4-chloro-2- methyl-phenoxyacetic acid either covalently or ionically bound to linear and cross leaked polymers are described poly (styrene/divinyl benzene) resins, cross linked polysaccharides, and homo and copolymers of oligo (oxyethylene) mono methacrylats were used as polymeric supports.

2-(Meth)acryloyloxy-2`,5-dichloro-4-nitrobenzonilide monomers were prepared(77) by reacting niclosamide with (meth)acryoyl chloride and polymerized to form polymeric moluscicides. Factors affecting niclosamide release rate by hydrolysis were investigated.

Smith et al.(78) prepared there polymers (polyacrylates, vinyl-alcohol, starch-based) and studies there controlled-release properties when expanded in urea, ammoniumsulfate and potassium nitrate solutions, at five nitrogen concentration (0, 10, 15, 20 g N/litre, and saturation). The expansion capacity (ml solution absorbed/g dry polymer) of each polymer varied and was dependent on the type and concentration of fertilizer solutions.

Issa et al.(79) studied a series of polymeric hydrogels containing different oxyethylene oligomers which prepared by radical polymerization of oligo (oxyethylene) methacrylate monomers in the presence of different amounts of N, N`-methylenebisacrylamide as crosslinking agent or acrylamide as hydrophilic comonomer systemic herbicides. Herbiocide release at room temperature in water at different pH values the release was affected by alkalinity and to a lesser extent by the polymer structure.

Rehab et al.(80) investigated two series of oligo (oxyethylene) methacrylats having different degrees of oligomerization. The two series of monomers, when submitted to radical polymerization give the corresponding homopolymers. A series of linear and cross linked polymeric herbiocides was also prepared by copolymerization of the

MCPA-containing dioxy ethylene octaoxyethylene monomethacrylat, acrylamide, methylene, bis acrylamide and 4-vinylpyridine all polymeric herbicides were tested for their release properting.

A series of alkyltin thioglycolats was syntheized by Fish(81), the structure and the equilibria with alkyltin chlorides was studied by infrared analysis. Dynamic Mechanical analysis was used to determine their compatibility with PVC.

Specific polymeric material applications as bioactive molecules delivery systems involve a strictly controlled degradation of polymer matrixes(82). One possibility to obtain azero-order kinetic for small molecules release consists in a simple hydrolysis of ester groups contained in the macromolecular structure. With the aim of antifualing applications, acrylic acid polymers bearing lateral ester groups of different chemical structure have been prepared, characterized and immersed in water, at pH (8) and their hydrolysis been studied.

Several organotin-amine molecular complexes have been synthesized(83) and evaluated as patent catalysis and accelerators for curing epoxy and epoxyanhydride resins. With epoxy-ahydride resin formulations the addition of approx. 0.10% of these for organotin amine complexes gives fast gel-cimes at 150-175 degree.

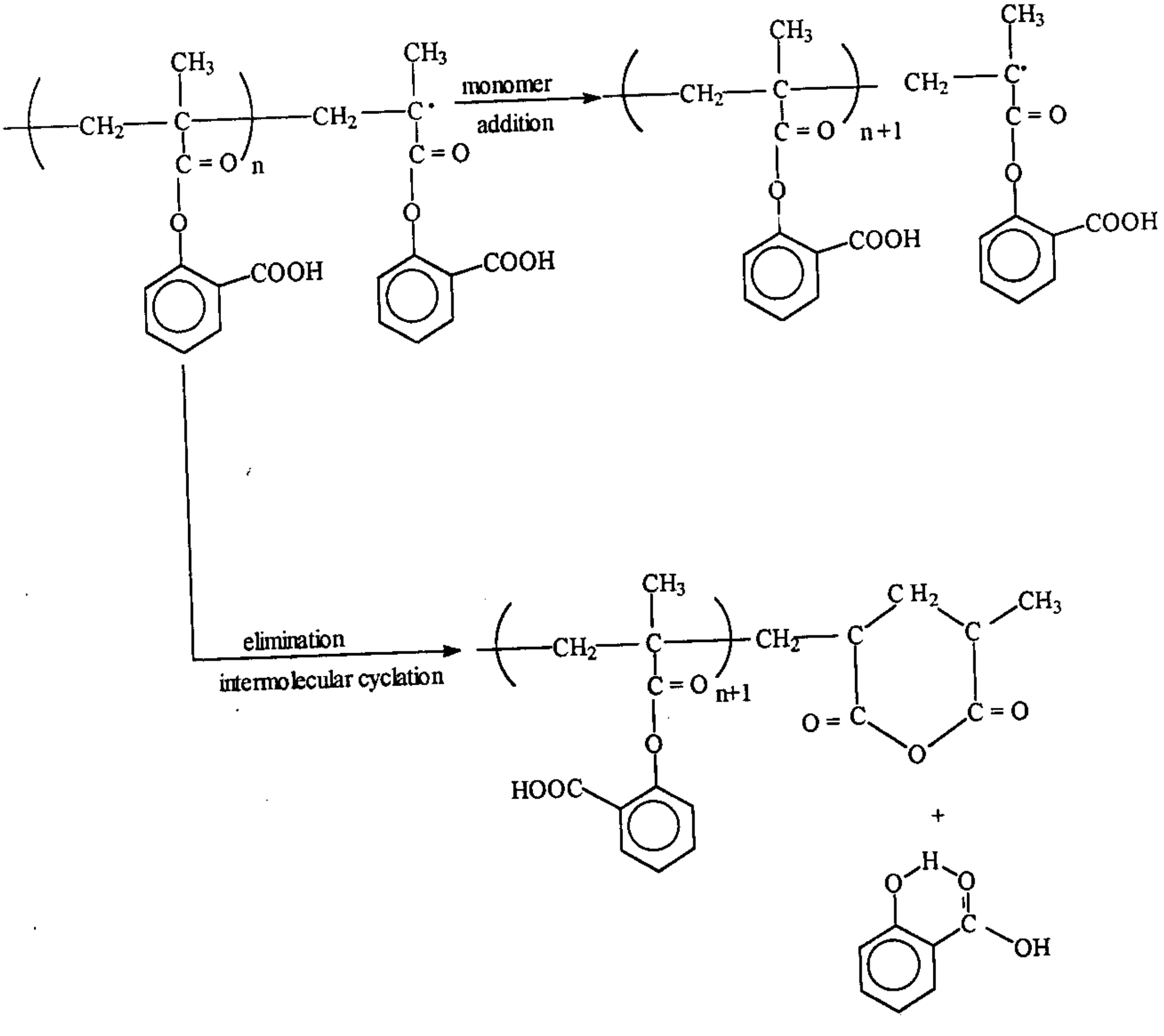
Shaaban et al.(84) studied the copolymerization reaction of di-(tri-n.butyltin) itaconate with methyl acrylate, ethylacrylate, n. butyl acrylate, 2-chloroethylacrylate, methyl methacrylate, allyl methacrylate, acrylonitrile, styrene and N-vinyl-2-pyrrolidinone. The copolymer composition of each sample was calculated from tin analysis. The monomer reactivity ratios for the systems studied were determined according to Fineman-

Ross and Kelen-Tudos methods. They also studied(85) the ternary copolymerization of di-(tri-n-bulytin) itaconate with acrylic acid esters styrene and acrylonitrile the experimental result for the azeotropic terpolymer composition were in good agreement with the theoretical values.

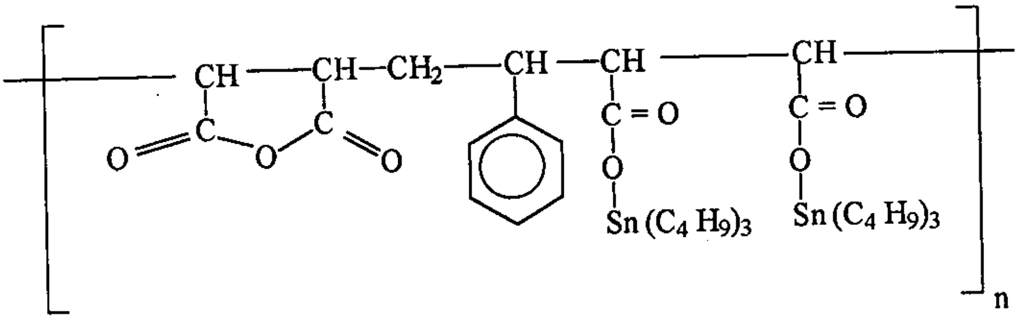
Han and Ring wold(86) showed that vinyl benzoate polymer and copolymers were invariably crosslinked gels, and they attributed this to the monomer being bifunctional, in that radicals could add to benzene ring as well as intiale normal polymerization through vinyl group. The slow rate of polymerization of vinyl benzoate was noted that no explanation presented. The highly branched and crosslinked structure of vinyl benzoate was also shows by Smet and Hertoghe(87), who hydrolyzed the polymer and observed the drop in the molecular weight which accompanied hydrolysis. This behaviour is consistent with Han and Ring wold's picture of branching through addition to the aromatic nuclei such links would be readily hydrolyzable.

Burnett and Wright(88) showed that the rate of polymerization was first order with respect to catalyst concentration or to the light intensity in case of photoinitiated polymerization. The monomer t.butyl-p-vinyl perbenzoate (TBVP) were prepared by Dalton and Tidwell(89) and it was homo-and copolymerization with styrene, methacrylonitrile, isopreme and phenylmethacrylate.

Rohan et al(90) prepared o-methacryloxy benzoic acid by the reaction of salicylic acid with methacrylchloride using potassium carbonate as catalyst and acetone as a solvent in the presence of little amount of hydroquinone. The polymerization of o-methacryloxy benzoic acid deviates from the classic free radical polymerization mechanism when the reaction is carried out in solution at moderatory high temperature. The mechanisms is characterized by two reactions in the propagation step, the addition of monomer unit to polymeric chain and the formation of anhydride group in the macromolecule chains as follows:

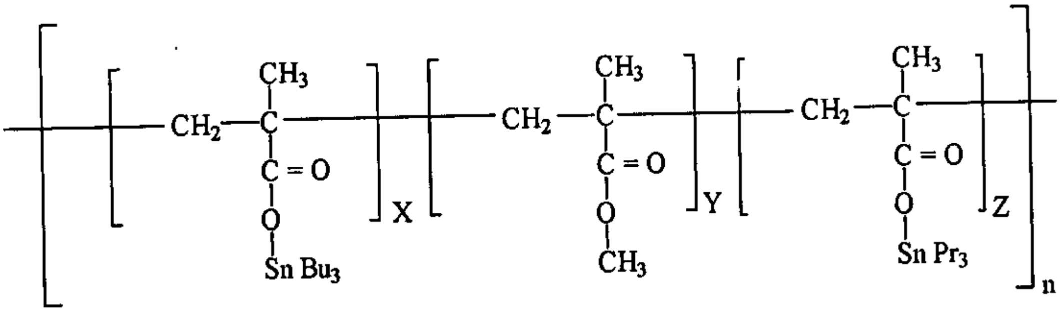


Kochkin and R.Zaev[(91)] studied aseries of Co-and terpolymers prepared from the reaction of maleic anhydride, styrene and organotin diester of maleic anhydride, with the following general structure.



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

Montemaraone and Dyckman(92) reported that the incorporation of such biocidal compounds in polymeric backbones, such as polymethacrylats, polystyrenes and polyesters, produced long lived, low-leaching orgamotin 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, non wettable, film forming and effective against bacteria, algae and fouling organisms. They also prepared organotin polymethacrylats based on tributyltin methancrylates with the following structure.



Zabotin and Malysheva(93) 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 for the copolymerzation reactions of tri-n.butyltinacrylate or methacrylate, n.propyl methacrylate, n.butylmethacrylate, allyl methacrylate, methyle acrylate, ethyl acrylate-n.butylacrylate, acrylnitrile and styrene were investigated(94) r_1r_2(95) 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 methacrylete or acrylic acid ester used.

Messiha(96) investigated the binary and ternary copolymerization reaction of tri-n.butyltin acrylate and methacrylate with vinyl acetate and N-vinylpyrrolidone. The monomer reactivity ratios obtained for the organotin monomers were much greater than the corresponding values of vinylacetate and n-vinyl pyrrolidone.

IKladious et al(97) determined the monomer reactivity ratios for the copolymerization reactions of tri-n.butyltinmeleate with methyl methacrylate, styrene, butyl acrylate and acrylonitrile.

The monomer reactivity ratios for the copolymerization reaction of triphenyltin methacrylate investigated(98,99). The sequence distribution of the alternating diad fractions for the systems studied were calculated at various feed compositions.

Shaaban et al(100,101) studied the copolymerzation reactions of N-acryloyloxyphthalimide and N-methacryloxyphthalimide with methyl acrylate, methyl methacrylate and acrylonitrile. The copolymer composition for each sample was calculated from ^{1}HNMR spectroscopy.