INTRODUCTION

CHAPTER I

INTRODUCTION

I. General Characterization

High polymers (or macromolecules) are substances of very high molecular weight, which may be natural or synthetic in origin and which have at least some element of structural regularity. This definition involves an enormous range of materials having widely different physical, chemical, and biological properties. Naturally occurring polymers include proteins and polysaccharides which form the structure of living tissues and provide the food supply for many life forms. Synthetic polymers find uses in almost every field of technology as structural and decorative materials, electrical and thermal insulators, paints, varnishes and adhesives, and in the textile industry, both as synthetic fibers and as coatings for natural fibers. Polymers have been synthesized which offer wide spectrum of physical properties ranging from hard, infusible resins to substances displaying rubber elasticity even at very low temperature.

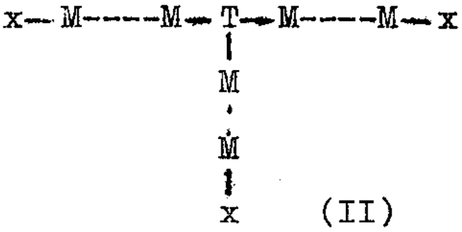
High polymers are composed of very large molecules, formed by linking together large numbers of simple chemical units (structural units). The structural units may be joined together in a variety of ways; in which simplest case the polymer may be represented by the formula (I) in which a simple, straight chain of n structural units (M) is terminated by two end groups x and y, which may be the same or different as:

$$x \{M\}_n\, y$$

(I)

The structural units of a polymer chain are normally closely related to the structure of the starting material or monomer from which the polymer is prepared. The simplest linear polymers are those in which all structural units are identical; such materials are called homopolymers, whilst polymers incorporating two or more chemically different types of structural units into the chain are termed copolymers. The majority of synthetic copolymers contain only two types of structural units and are therefore termed binary copolymers.

If, however, some of the monomer molecules are trifunctional, i.e. capable of bonding to three other units, then the polymer may have a non-linear structure which may be represented as follows :



$$\begin{array}{c} x - M - - - - M - T - M - - - - M - x \\ | \\ M \\ \vdots \\ M \\ | \\ x \end{array}$$

(II)

A polymer of this form, in which the structural units of the side chain are identical to those of the main chain (or backbone), is said to be branched. If the side-chains of a branched polymer are formed from structural units which are different from those of the backbone, the polymer is termed a graft copolymer. The presence of trifunctional units in a polymer chain allows wide variations in molecular geometry, for example a side chain in a branched polymer may be terminated either with a monofunctional end-group, or by reaction with a 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 threedimensional. The formation of threedimensional networks during polymerization results in a cross-linked network 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.

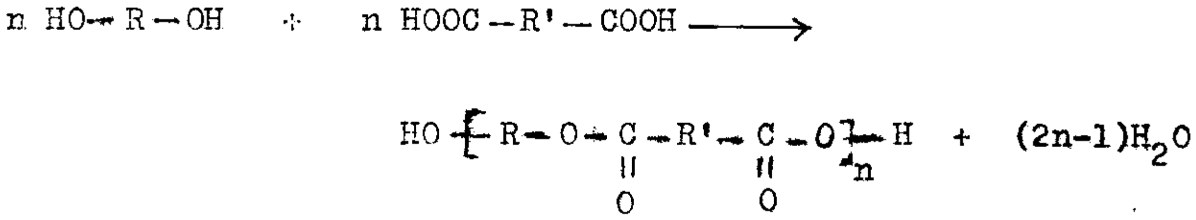
2. Classification of Polymers

Carothers[1] classified all polymers into two types:

a: Condensation polymers.

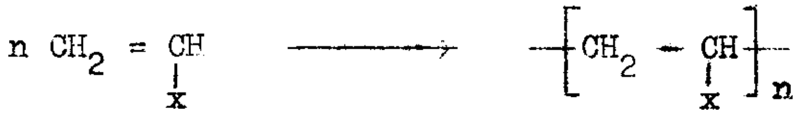
b. Addition polymers.

A condensation polymer is one which does not have the same composition as the monomer or monomers from which it was formed or to which it may be degraded by chemical means. These polymers are formed from bi- or poly-functional monomers with the elimination of some smaller molecules as a by-product, such as water, methanol, hydrogen chloride, etc... For example, a polyester is formed by typical condensation reaction between bi-functional monomers, with the elimination of water,



$$n\ HO-R-OH + n\ HOOC-R'-COOH \longrightarrow HO\left[R-O-\underset{\underset{O}{\|}}{C}-R'-\underset{\underset{O}{\|}}{C}-O\right]_n H + (2n-1)H_2O$$

An addition polymer is one in which the recurring units have the same composition as the monomers from which they are formed. These polymers are formed from bi- or poly-functional monomers by the addition of one monomer to another without the loss of any portion of the monomer. The polymerisation of vinyl monomers is an example of this class.



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

In most vinyl polymerizations, if polymerization is stopped at any instant and the polymer examined, it is found that the mixture consists of unchanged monomer and high molecular-weight polymer. This general picture contrasts sharply with that existing in polycondensation reactions, in which all of monomers has to be converted to low molecular-weight oligomers before polymerization progresses to give high molecular weight products.

3. Free Radical addition polymerization

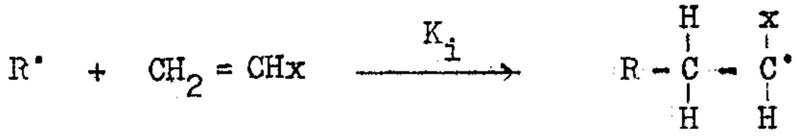
Free radical addition polymerization is a very powerful method for the preparation of polymers from a wide variety of unsaturated vinyl, vinylidene and diene monomers and is one of the most widely used industrial methods for the manufacture of addition polymers.

Mechanisms of free radical polymerization

Addition polymerization by mechanisms involving free radicals as chain carriers requires the normal steps of initiation, propagation, and termination, typical of all chain reactions.

1. Initiation

Initiation of a radical polymerization requires the creation of radicals capable of reaction with the monomer:

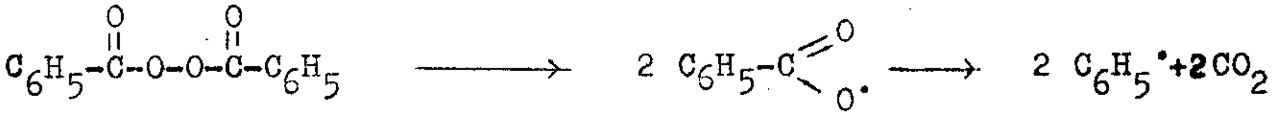


$$R^{\cdot} + CH_2 = CHx \xrightarrow{K_i} R-\overset{H}{\underset{H}{C}}-\overset{x}{\underset{H}{C^{\cdot}}}$$

A number of methods are available for this process. Direct thermal initiation of some monomers (especially styrene) can be used. The mechanisms by which thermal initiation occurs are not very well understood. High energy radiation, is often effective in initiating polymerization but these methods are difficult to control and in many cases lead to ionic rather than radical reactions. In the vast majority of practical polymerizations, radical production is brought about by thermal or photochemical breakdown of an added initiator. A wide variety of substances are employed as initiators but they mostly fall into one of the following three groups:

(a) Peroxides and hydroperoxides

Many organic peroxides and hydroperoxides are thermally unstable and decompose to produce radicals which are capable of initiating polymerization. In the temperature range 35-80°C radicals are easily generated by the thermal breakdown of benzoyl peroxide, which is one of the most widely used initiators for vinyl polymerization:



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2\ C_6H_5-C\genfrac{}{}{0pt}{}{\diagup\!\!\diagup O}{\diagdown O^{\cdot}} \longrightarrow 2\ C_6H_5^{\cdot} + 2CO_2$$

This reaction is a two-stage process (Barson and Bevington, 1956)[2]. Its kinetics are not accurately first order and the rate of decomposition varies considerably with the solvent employed for the reaction. For these reasons, the use of benzoyl peroxide may create complications in detailed studies of polymerization kinetics and other initiators are often preferred.

(b) Azo initiators

Radicals may be generated by the thermal or photochemical rupture of aliphatic azo-nitriles and related compounds. The most common example of this type of initiators is azo-bis-isobutyronitrile:

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

The decomposition of this compound is accurately first order (Lewis and Matheson 1949)[3] and the rate is much less affected by changes in solvent than is the decomposition of benzoyl peroxide. Thus, azo-bis-isobutyronitrile is very frequently used as an initiator for research studies on radical polymerization.

(c) Redox initiators

Al low temperatures, free-radicals are conveniently generated by redox initiators (Bacon 1955)[4]. In such systems initiation takes place as a consequence of an oxidation-reduction reaction between two initiator components. One common redox system is the combination of an alkyl or aryl peroxide or hydroperoxide with an oxidizable metal ion in its reduced state:

$$R-O-O-R \quad + \quad M^{2+} \longrightarrow M^{3+} \quad + \quad RO^{\bullet} \quad + \quad RO^{-}$$

Polymerization in aqueous media is readily initiated by thermal fission of persulphates, e.g. $K_2S_2O_8$, as follows:

$$S_2O_8^{-2} \longrightarrow 2\ SO_4^{\bullet}$$

The initiation rates achieved in using persulphates may be increased by the use of a second catalyst component to provide a redox system. Typical accelerators of persulphate decomposition include metal ions in low oxidation states,

$$Fe^{2+} \quad + \quad S_2O_8^{2-} \longrightarrow Fe^{3+} \quad + \quad SO_4^{2-} \quad + \quad SO_4^{\bullet}$$

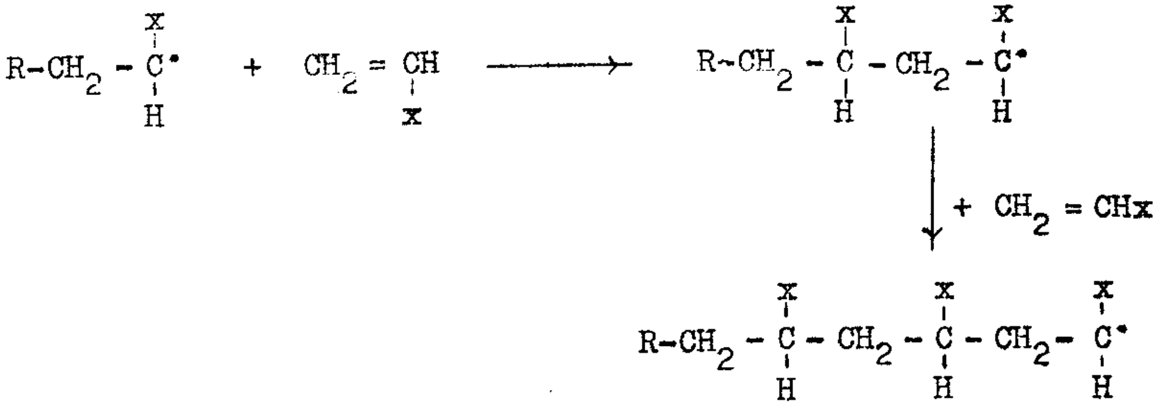
and bisulphite ions:

$$S_2O_8^{2-} \quad + \quad HSO_3^{-} \longrightarrow SO_4^{2-} \quad + \quad SO_4^{\bullet} \quad + \quad HSO_3^{\bullet}$$

Particularly important are the redox reactions commonly occurring in aqueous media involving electron transfer processes.

2. 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 monomer molecules are successively added to continuously propagate the reactive center:



$$R-CH_2-\overset{x}{\underset{H}{C^\bullet}} + CH_2=\underset{x}{CH} \longrightarrow R-CH_2-\overset{x}{\underset{H}{C}}-CH_2-\overset{x}{\underset{H}{C^\bullet}} \xrightarrow{+\ CH_2=CHx} R-CH_2-\overset{x}{\underset{H}{C}}-CH_2-\overset{x}{\underset{H}{C}}-CH_2-\overset{x}{\underset{H}{C^\bullet}}$$

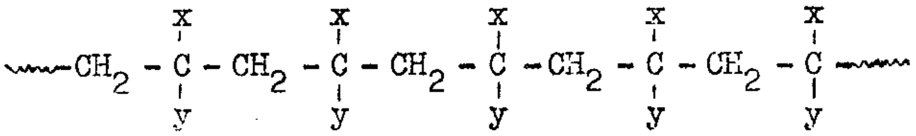
There are two possible points of attachment on monosubstituted (x = H) or 1-1-disubstituted monomers for a propagating radical either on carbon 1 or carbon 2 :

$$R^\bullet + \overset{x}{\underset{y}{C}}=CH_2 \longrightarrow R-\overset{x}{\underset{y}{C}}-CH_2^\bullet \qquad (1)$$

or

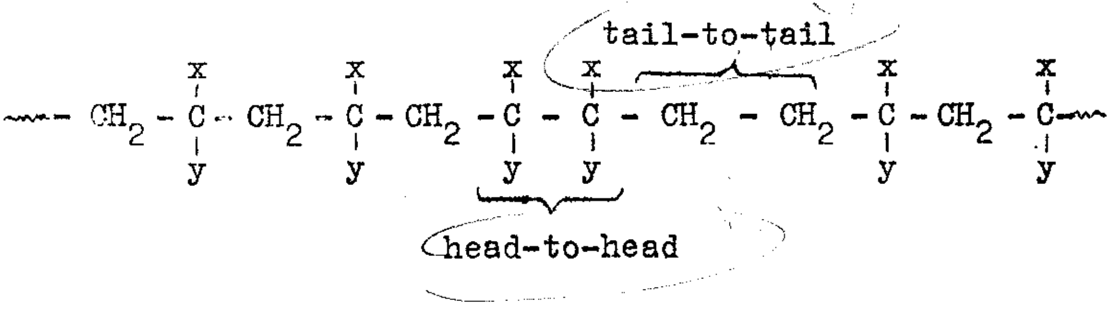
$$R^\bullet + \overset{x}{\underset{y}{C}}=CH_2 \longrightarrow R-CH_2-\overset{x}{\underset{y}{C^\bullet}} \qquad (2)$$

If each successive addition of monomer molecules to the propagating radical occurs in the same manner as equation 2, the final polymer product will have an arrangement of monomer units in which the substituents are on alternate carbon atoms:



$$\sim CH_2-\underset{y}{\overset{x}{C}}-CH_2-\underset{y}{\overset{x}{C}}-CH_2-\underset{y}{\overset{x}{C}}-CH_2-\underset{y}{\overset{x}{C}}-CH_2-\underset{y}{\overset{x}{C}}\sim$$

This type of arrangement is usually referred to as a head-to-tail of monomer units. An inversion of this mode of addition of the polymer chain propagating alternatively via equation 2 and 1 would lead to a polymer structure with 1,2- placement of substituents at one or more places in final polymer chain which is variously termed head-to-head placement or tail-to-tail placement. The head-to-tail placement would be expected to predominate.



$$\sim CH_2-\underset{y}{\overset{x}{C}}-CH_2-\underset{y}{\overset{x}{C}}-CH_2-\underbrace{\underset{y}{\overset{x}{C}}-\underset{y}{\overset{x}{C}}}_{\text{head-to-head}}-\overbrace{CH_2-CH_2}^{\text{tail-to-tail}}-\underset{y}{\overset{x}{C}}-CH_2-\underset{y}{\overset{x}{C}}\sim$$

3. Termination

Termination of growing polymer chains may occur in a number of ways:

(a) By recombination of two growing chain radicals, resulting in the formation of "head-to-head" linkage as:

$$R-\left[CH_2-CHx\right]_n CH_2-CHx^{\bullet} + {}^{\bullet}xHC-CH_2-\left[CHx-CH_2\right]_m R \longrightarrow$$

$$R-\left[CH_2-CHx\right]_{n+1}-\left[xHC-CH_2\right]_{m+1} R$$

(b) By disproportionation between two growing chain radicals, in which 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.

$$R-\left[CH_2-CHx\right]_n CH_2-CHx^{\bullet} + {}^{\bullet}xHC-CH_2-\left[CHx-CH_2\right]_m R \longrightarrow$$

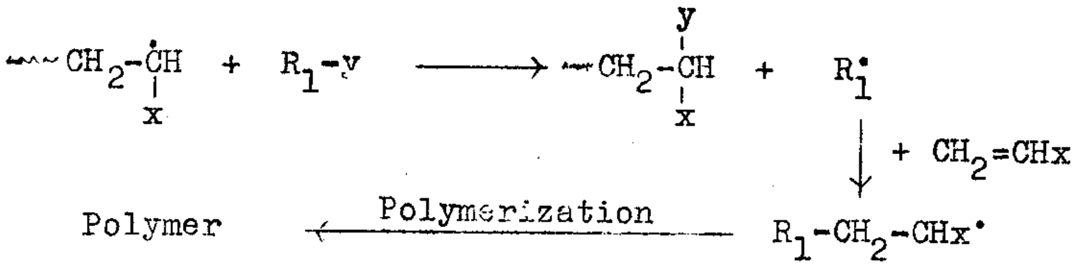
$$R-\left[CH_2-CHx\right]_n CH_2-CH_2x + xHC{=}CH-\left[CHx-CH_2\right]_m R$$

(c) By recombination of growing chain radical with the primary radical derived from the initiator:

$$R-\left[CH_2-CHx\right]_n CH_2-CHx^{\bullet} + R^{\bullet} \longrightarrow R-\left[CH_2-CHx\right]_{n+1} R$$

Chain transfer

A growing chain radical may abstract an atom 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:



$$\sim CH_2-\underset{x}{\overset{\bullet}{C}H} + R_1-y \longrightarrow \sim CH_2-\underset{x}{\overset{y}{CH}} + R_1^\bullet$$

$$R_1^\bullet \xrightarrow{+\ CH_2=CHx} R_1-CH_2-CHx^\bullet$$

$$\text{Polymer} \xleftarrow{\text{Polymerization}} R_1-CH_2-CHx^\bullet$$

Chain transfer of this type may occur with initiator, the solvent or other compounds which have been added in order to promote chain transfer, and with growing or complete polymer chains. Among the common initiators, the hydroperoxides as t-butylhydroperoxide or cumene-hydroperoxide are the ones with a tendency to transfer reactions, whereas benzoyl peroxide, and especially azo-bis-isobutyronitrile, do not take part in transfer reactions.

4. Kinetics of radical polymerization

If we denote a primary radical, derived from the decomposition of the initiator, by $R^\bullet$ and a propagating radical having n monomer units by $P_n^\bullet$ then we may write the following kinetic scheme for radical polymerization in the absence of transfer reactions:

$$\left.\begin{array}{l} \text{Initiator} \xrightarrow{K_D} 2\ R^\bullet \\ R^\bullet + M \xrightarrow{K_i} P_1^\bullet \end{array}\right\} \text{Initiation}$$

$$P_n^\bullet + M \xrightarrow{K_P} P_{n+1}^\bullet \qquad \text{Propagation}$$

$$P_n^\bullet + P_m^\bullet \xrightarrow{K_t} \text{Polymer} \qquad \text{Termination}$$

The rate of generation of active centres $P_1^{\bullet}$ is taken as I, and K_t is the sum of the rate constants for termination by combination and disproportionation; primary radical termination is neglected since its effect is noticeable only at high initiator or low monomer concentrations. In order to treat the kinetics of this reaction scheme in any simple way, it is necessary to assume that the propagation rate may be defined by one single rate-constant K_p. For the reaction scheme under consideration, we may write:

$$-d[M]/dt = K_p [P^{\bullet}][M] + K_i [R^{\bullet}][M] \qquad (1)$$

If, as in most practical cases, the rate of consumption of monomer by propagation is very much greater than that by initiation, the rate equation simplifies to :

$$-d[M]/dt = K_p [P^{\bullet}][M] \qquad (2)$$

The final assumption which we shall make in this treatment is known as the stationary-state approximation. It is assumed that the rate of change of the concentration of radicals in the system is very much lower than the rate of consumption of monomer, i.e.,

$$\left| d[P^{\bullet}]/dt \right| \ll \left| d[M]/dt \right| \qquad (3)$$

This criterion is normally expressed by stating that $d[P^{\bullet}]/dt$ can be set equal to zero, i.e. that radicals are created in the initiation step at a rate equal to that with which they are destroyed by termination. Thus we have :

$$d\,[P^\cdot]/dt \;=\; I - K_t\,[P^\cdot]^2 \;=\; 0 \qquad (4)$$

where $I = 2fK_D\,[\text{Initiator}]$, f being the initiator efficiency. Hence,

$$[P^\cdot] \;=\; (I/K_t)^{1/2}$$

So that by substitution in equation (2) we obtain :

$$-\,d[M]/dt \;=\; K_p/K_t^{1/2}\,.\,[M]\,.\,I^{1/2} \qquad (5)$$

Polymerization equation (5) describes the most common case of radical chain polymerization and should apply to the initial stages of radical polymerization. It shows that from equation (5) the order of reaction respect to the monomer concentration is a first order and one-half order respect to the initiator concentration. This dependence has been confirmed for many different monomer-initiator combinations over wide ranges of monomers and initiators[5-8]. Deviation from this behaviour are found under certain conditions[9].

5. 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 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 monomers whose homopolymers are rubber like, such as vinyl ether or acrylic 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 mechanism, are often used as the components of a copolymerization and then copolymerize by a radical mechanism.

Copolymer composition equation

The composition of the copolymer molecules which are forming at a given time in a mixture of two monomers depends on the relative rates with which the two kinds of monomer units enter a copolymer molecule. When the rate at which a monomer adds to the polymer chain depends only on the monomer unit at the end of the chain and not on the next-last monomer unit (penultimate), the composition of the copolymer is determined by the molar composition of the mixture of monomers and by the rate constants of the following four reactions[10,11]:

$$\sim\!\sim M_1^{\cdot} + M_1 \xrightarrow{K_{11}} \sim\!\sim M_1M_1^{\cdot} \qquad (1)$$

$$\sim\!\sim M_1^{\cdot} + M_2 \xrightarrow{K_{12}} \sim\!\sim M_1M_2^{\cdot} \qquad (2)$$

$$\sim M_2^{\bullet} \quad + \quad M_2 \quad \xrightarrow{K_{22}} \quad \sim M_2M_2^{\bullet} \tag{3}$$

$$\sim M_2^{\bullet} \quad + \quad M_1 \quad \xrightarrow{K_{21}} \quad \sim M_2M_1^{\bullet} \tag{4}$$

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. The composition of the copolymer that is formed could be related to the concentration of the two monomers in the feed as follows :

From the copolymerization reactions (1-4), M_1 and M_2 are used in the reactions as :

$$-\ d[M_1]/dt \quad = \quad K_{11}[M_1^{\bullet}][M_1] \ + \ K_{21}\,[M_2^{\bullet}][M_1] \tag{5}$$

$$-\ d[M_2]/dt \quad = \quad K_{22}[M_2^{\bullet}][M_2] \ + \ K_{12}\,[M_1^{\bullet}][M_2] \tag{6}$$

The ratio of the amounts of the two monomers incorporated into the copolymer in an infinitisimal period of time is given by dividing equation (5) by equation (6) to get :

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{K_{11}\,[M_1^{\bullet}]/[M_2^{\bullet}] + K_{21}}{K_{12}\,[M_1^{\bullet}]/[M_2^{\bullet}] + K_{22}} \tag{7}$$

The ratio K_{11}/K_{12} and K_{22}/K_{21} are defined by r_1 and r_2, respectively, and termed the monomer reactivity ratios which measure the relative affinities of different monomers for the two extremes of ideal and alternating behaviour. The alternation tendency 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 an azeotropic composition at which the copolymer and the feed compositions are the same, and the copolymerization occurs without change in the feed composition to give :

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}$$

by substitution in equation 9 (page 17) one gets :

$$F_1 = f_1 = \frac{1-r_2}{2-r_1-r_2} \qquad (13)$$

(c) when $r_1r_2 > 1$, this is a rare case and if it exists, it leads to the synthesis of blocks of copolymers or a mixture of the homopolymers.

Methods of calculating monomer reactivity ratios

All methods for the determination 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 labelling and ultraviolet, infrared and nuclear magnetic spectroscopy.

All procedures depend on copolymerizations carried out to low degrees of conversions (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[11], depends on the copolymerization equation (equation 8, page 17), which can be expressed in terms of molar ratios instead of concentration as[13] :

$$b = \frac{r_1 a + 1}{r_2/a + 1}$$

where a and b are the molar ratios of the comonomers in the feed and copolymer respectively. In this method for each single copolymerization result, r_1 is allowed to take a selected value in the copolymerization equation, and r_2 is plotted as a function of r_1. The straight lines corresponding to each experimental result should intersect at a common point giving the r_1 and r_2 values.

(b) Fineman-Ross method

Fineman and Ross[14] were the first who arrange the differential copolymer composition equation in the following form:

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

a-a/b as the ordinate against a^2/b as abcissa, the slope of the straight line is r_1 and the intercept is $-r_2$. When the polymer composition measurements are precise, this method is very convenient and frequently used due to its simplicity and accuracy.

(c) Joshi-Kapur method[15] [illegible] R. M. Joshi

This method is published in 1954 with a view to eliminating subjective error in the location of the best point in the intersection method of Mayo-Lewis plot.

(d) Tidwell-Mortimer method P. W. Tidwell

In detailed critical treatises, Tidwell and Mortimer[16] pointed out the defects of the different methods, and suggested a standard computerized procedure; the 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 that the absolute error in the copolymer composition is independent of its value or constant.

(e) Yezrielev-Brokhina-Roskin method

Yezrielev, Brokhina and Roskin[17] transformed the linear equation of copolymer composition into the symmetrical form as:

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

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

and $b = M_1/M_2$ (molar ratio of of the two monomers 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

This is the **most** recent method published by Kelen and Tüdős[18] for calculating the monomer reactivity ratios based on a new graphically evaluable linear equation as follows:

$$\eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_2}{\alpha}$$

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

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 $\xi = 1$ gives $-r_2/\alpha$ and r_1 respectively (both as intercepts).

Factors affecting monomer reactivity ratios

With respect to free-radical copolymerization, it may be stated that reactivity ratios are comparatively little influenced by most common variables such as conversion, solvent and method of polymerization[19]. In the range of temperatures from room temperature to about 100°C there is little variation in reactivity ratios in binary copolymerizations. However, there is a tendency for the r_1r_2 product to approach 1 as temperature increases. Copolymerization has been affected at temperatures as -78°C and temperatures 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 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 homogeneous system, that is the precipitation of copolymers 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[20], the product of r_1r_2 increased from 0.16 (at atmosphere pressure) to 0.91 (at 1000 atmosphere) indicating that increased pressure increases the tendency for this system towards blocks.

Terpolymer composition equation

Chemists sometimes polymerize mixture of three (or more) monomers with the intent of preparing multicomponent polymers that will have the properties required for a specific use. The commercial importance of multicomponent polymerization has rapidly increased in the last decade. Incorporation of a third monomer developed gross effects on the properties of copolymers such as heat resistance, tensile strength, elasticity, transparency and solvent resistance. It is desirable to know the relationship between the ratio of a given set of monomers and the corresponding copolymer composition. It has been shown by Alfery and Goldfinger[21] that there are nine propagation reactions in determination terpolymer composition:

$$\begin{array}{l|l|l}
\sim M_1^{\bullet}+M_1 \xrightarrow{K_{11}} \sim M_1M_1^{\bullet} & \sim M_2^{\bullet}+M_1 \xrightarrow{K_{21}} \sim M_2-M_1^{\bullet} & \sim M_3^{\bullet}+M_1 \xrightarrow{K_{31}} \sim M_3-M_1^{\bullet} \\
\sim M_1^{\bullet}+M_2 \xrightarrow{K_{12}} \sim M_1-M_2^{\bullet} & \sim M_2^{\bullet}+M_2 \xrightarrow{K_{22}} \sim M_2-M_2^{\bullet} & \sim M_3^{\bullet}+M_2 \xrightarrow{K_{32}} \sim M_3-M_2^{\bullet} \\
\sim M_1^{\bullet}+M_3 \xrightarrow{K_{13}} \sim M_1-M_3^{\bullet} & \sim M_2^{\bullet}+M_3 \xrightarrow{K_{23}} \sim M_2-M_3^{\bullet} & \sim M_3^{\bullet}+M_3 \xrightarrow{K_{33}} \sim M_3-M_3^{\bullet}
\end{array}$$

In order to predict the behaviour of a three- component system (M_1-M_2-M_3), it is necessary to know the copolymerization parameters of the three separate two-component copolymerization as follows:

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

In a manner completely analogous to that described for two component systems (page 15) 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:

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

$$: \left[M_2\right]\left[\frac{\left[M_1\right]}{r_{12}r_{31}} + \frac{\left[M_2\right]}{r_{12}r_{32}} + \frac{\left[M_3\right]}{r_{32}r_{13}}\right]\left[\left[M_2\right] + \frac{\left[M_1\right]}{r_{21}} + \frac{\left[M_3\right]}{r_{23}}\right]$$

$$: \left[M_3\right]\left[\frac{\left[M_1\right]}{r_{13}r_{21}} + \frac{\left[M_2\right]}{r_{23}r_{12}} + \frac{\left[M_3\right]}{r_{13}r_{23}}\right]\left[\left[M_3\right] + \frac{\left[M_1\right]}{r_{31}} + \frac{\left[M_2\right]}{r_{32}}\right]$$

Terpolymerization composition equation has been tested by a number of workers and has been found to describe experimental copolymerization within the limits to be expected from the accuracy of the reactivity values 22-24.

Ham[25] proposed a simpler 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 :

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

and the terpolymer composition equation was simplified in the form :

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

Mayo[26] reported that Ham's equation is potentially useful for bringing out inconsistencies between experimental data are theoretical correlations and prediction of behaviours of monomers in copolymerizations. Also, Ham's probabilities are sometimes quite good and sometimes very poor.

Khan and Horowitz[27] studied the terpolymerization of vinyl acetate-dioctyl fumarate-N-vinyl pyrrolidone system and programed the differential terpolymer composition equation on a digital computer in the following form :

$$
\begin{aligned}
&d\,M_1 : d\,M_2 : d\,M_3 = \\
&M_1\left[M_1r_{23}r_{32} + M_2r_{31}r_{23} + M_3r_{32}r_{21}\right]\left[M_1r_{12}r_{13} + M_2r_{13} + M_3r_{12}\right] : \\
&M_2\left[M_1r_{32}r_{13} + M_2r_{13}r_{31} + M_3r_{12}r_{31}\right]\left[M_2r_{21}r_{23} + M_1r_{23} + M_3r_{21}\right] : \\
&M_3\left[M_1r_{12}r_{23} + M_2r_{13}r_{21} + M_3r_{12}r_{21}\right]\left[M_3r_{31}r_{32} + M_1r_{32} + M_2r_{31}\right]
\end{aligned}
$$

Organotin Polymers

Since 1950, systematic investigations have been carried out on organotin compounds as biocides. There is a current trend away from the use of organolead and organomercury compounds due to their high mammalian toxicity and their relatively adverse effects on the environment. Organotin compounds are even eventually degraded in nature to give non-toxic inorganic tin residues[28]. The action of organotin compounds towards fungi, bacteria, marine organisms, parasitic worms, aquatic snails and insects have been studied. The most important of these is undoubtedly the use of organotin compounds as fungicides in agriculture, application in antifouling caotings, and wood preservation.

Montemarano and Dyckman[29] reported that the incorporation of such biocidal organotin compounds on 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.

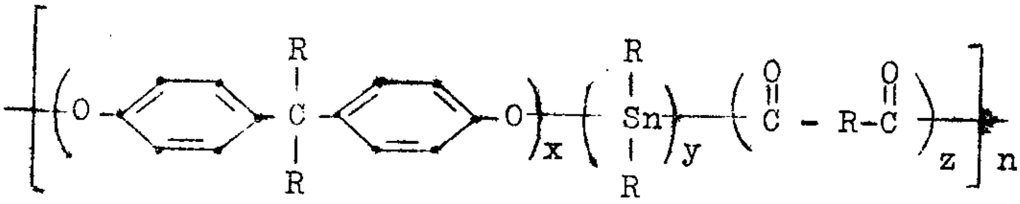
The literature dealing with organotin polymers is not extensive due to the secrecy which surrounds its most applications. Organotin polymers may be classified as substances containing tin atoms, bound to carbon, in the main chain or pendent in side chains.

a) Tin atoms in polymer main chain

Generally, the synthesis of polymers containing tin atoms in the polymer backbone are 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 :

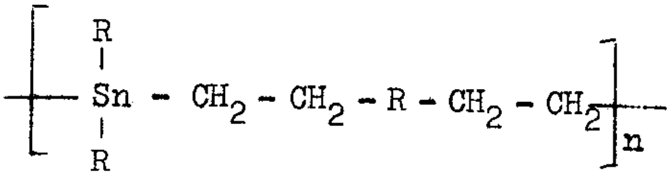
$$R_2SnCl_2 + R'(COONa)_2 \longrightarrow \left[Sn(R_2)OOCR'COO \right]_n + 2NaCl$$

Alternatively, organotin diacetates or dibutyltin oxide can be reacted with diacids to form similar products[30], which were characterized by a lower order of polymerization due in part to cyclization reactions. Also, the condensation products of a bisphenol and a mixture of a diorganotin dihalide and acyl halide of a dicarboxylic acid were reported[31] to be linear chain as follows :



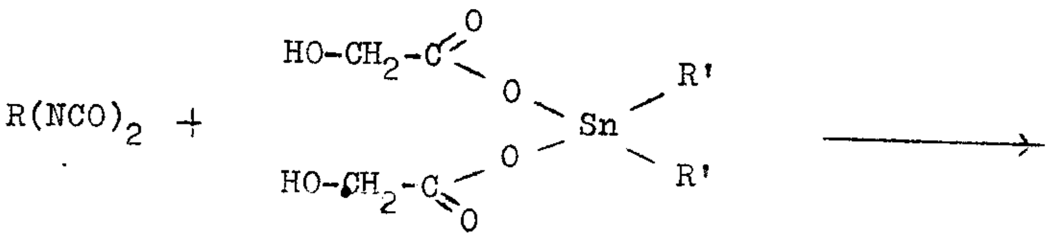
Noltes and Van der Kerk[32] studied the reactions involving organotin dihydrides and diolefins to prepare organotin polymers of the type :

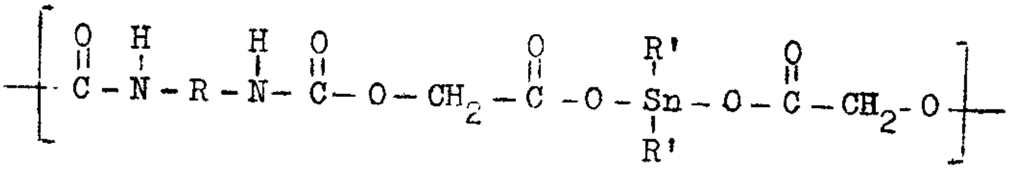
$$R_2SnH_2 \quad + \quad CH_2 = CH - R - CH = CH_2 \quad \longrightarrow$$



$$\left[-\overset{R}{\underset{R}{Sn}} - CH_2 - CH_2 - R - CH_2 - CH_2 - \right]_n$$

Another route to the synthesis of polyesters having tin in the polymer backbone has been described by Leebrick[33], who prepared polyurethanes containing tin as follows :





$$-\!\!\left[\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{O}{\overset{\|}{C}}-O-\underset{R'}{\underset{|}{\overset{R'}{\overset{|}{Sn}}}}-O-\overset{O}{\overset{\|}{C}}-CH_2-O\right]\!\!-$$

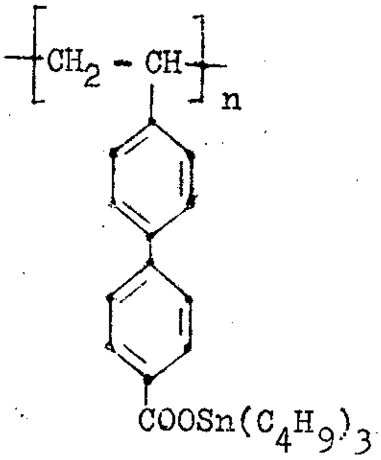
b) <u>Tin atoms pendent to polymer chain</u>

Polymers containing organotin groups pendent to a carbon backbone are generally obtained by free radical initiated polymerizations of unsaturated organotin ester monomers. Montermoso et al[34] prepared a series of monomers through the reaction of organotin oxides or hydroxides with unsaturated acids as follows :

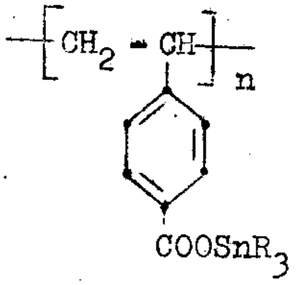
$$(R_3Sn)_2O \;+\; 2\,R'CH{=}CR''\text{-}COOH \longrightarrow 2\,R'CH{=}CR''COOSnR_3 \;+\; H_2O$$

where R, R' and R" = H, alkyl or aryl. These unsaturated organotin monomers could also be prepared by the reaction of organotin halides[35] or tetraryltins with the unsaturated organic acid. A considerable number of organotin polyacrylates have been prepared from their respective monomers, and polymerized using bulk, solution and emulsion polymerizations; which may find application as films, foils and coatings[34].

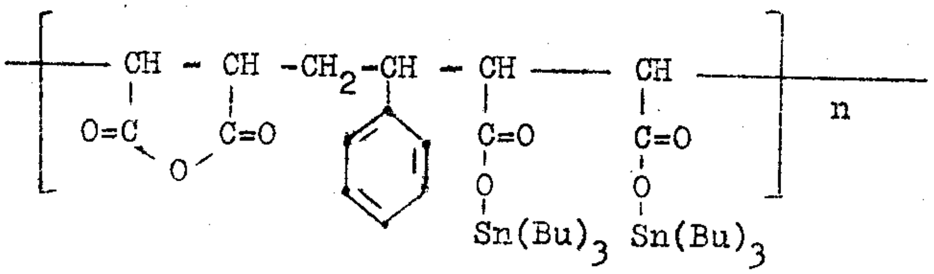
Adrova et al[36] prepared poly tributyltin-4'-vinyl-4-biphenyl carboxylate and reported it to be colourless soluble polymer, stable at 165°C, as :



Similarly, Leebrick [37] prepared an analogous series of polymers based upon vinyl benzoic acid as illustrated below :

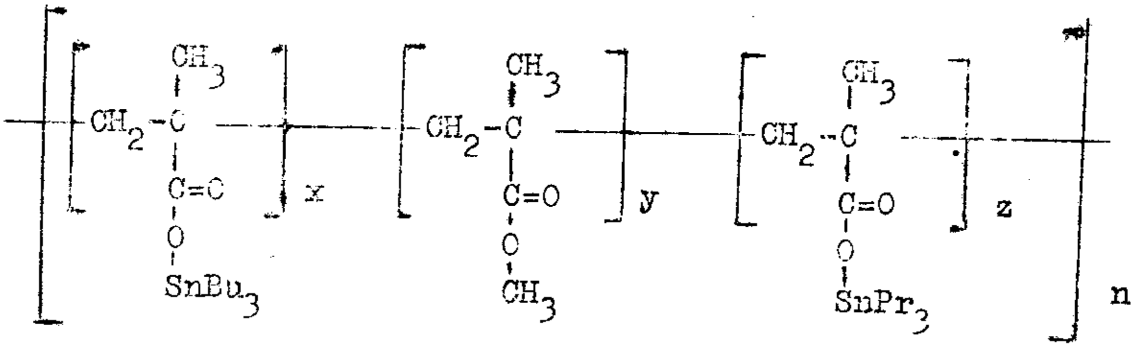


Kochkin[38] and Rzaev[39] studied a series of co- and ter-polymers prepared from the reaction of maleic anhydride, styrene and organotin diester of maleic anhydride, with the following general structure :



These polymers were found to be resistant to ultraviolet aging and have bactericidal and general anti-microbial behaviour.

Montemarano and Dychman[29] prepared organotin polymethacrylates based on tributyltin methacrylate and tripropyltin methacrylate with the following general structure :



$$-\left[\left[-CH_2-\overset{\displaystyle CH_3}{\underset{\begin{array}{c}|\\C=O\\|\\O\\|\\SnBu_3\end{array}}{C}}-\right]_x\left[-CH_2-\overset{\displaystyle CH_3}{\underset{\begin{array}{c}|\\C=O\\|\\O\\|\\CH_3\end{array}}{C}}-\right]_y\left[-CH_2-\overset{\displaystyle CH_3}{\underset{\begin{array}{c}|\\C=O\\|\\O\\|\\SnPr_3\end{array}}{C}}-\right]_z\right]_n-$$

They studied the toxin release of such copolymers and reported that tributyltin methacrylate-methyl methacrylate copolymer released 45 % less organotin ions than polytributyltin methacrylate, indicating that the degree of leaching from an organometallic polymer may be controlled by chemical modification of its polymer matrix. Therefore, the optimal effective material exhibiting a minimal amount of leaching can be produced by varying the ratio of organometallic monomer to inert comonomer along the copolymer backbone.

Evans et al.[28], working on the same subject, reported that the incorporation of two R_3Sn groups such as tributyl- and tripropyltins, into a polymeric network widens the spectrum of effectiveness but would otherwise prove too toxic for general use.

Fujitani[40] prepared emulsions of organotin polymers, for use as antifouling paints, by terpolymerization of triphenyltin methacrylate, methyl methacrylate and ethyl acrylate.

Also, antifouling paints formulations based on allyl 2,4 - dichlorophenoxy acetate- butyl acrylate- tributyltin acrylate terpolymer were prepared and tested by Matsuda et al[41].

Atherton and co-workers[42] examined copolymers prepared from tributyltin methacrylate with methyl methacrylate, styrene and butyl acrylate, 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.

No much work has been done to study the kinetics and copolymerisation parameters of organotin monomers to illustrate the composition and distribution of the organotin moiety within the copolymer chains. However , in a comparison study Koton[43] noted that triphenyltin methacrylate polymerizes more rapidly than methyl methacrylate.

Copolymers of p-triphenyltin styrene and styrene or vinyl toluene, were prepared and studied kinetically by Sandler et al[44], 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 units should be present in the polymer network.

Zabotin and Malysheva[45] studied the copolymerizations of tributyltin acrylate with alkyl acrylates 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[46] who reported that the copolymer produced could be self-cured to a crosslinked product by heating.

Mode of action of organotins

It may be stated that only very few organotin compounds[47], e.g. triethyltin salts are highly toxic and the 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 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.

Aim of the Present Work

Organotin compounds find widespread applications as biocides against bacteria, fungi, aquatic snails, marine organisms and insects. The incorporation of organotin compounds onto polyacrylates or polymethacrylates produces long-lived effective organotin polymers that reduces the pollution hazards attributed to toxins. It is evident that the physical properties of organotin polymers and copolymers is greatly affected by the organotin moiety in the polymer chain. Also, the biocidal efficiency of such organotin polymers is influenced by the composition and distribution of the organotin monomer in the copolymer matrix. In spite of the great practical interest of polymers and copolymers containing tin, no much work has been done concerning the kinetics and copolymerization behaviours of organotin monomers. Thus, in the present work tri-n-butyltin acrylate and tri-n-butyltin methacrylate monomers were prepared through the reaction of tri-n-butyltin oxide with acrylic or methacrylic acids, respectively. It was aimed to determine the copolymerization parameters and to discover any azeotropy of these organotin monomers with alkyl methacrylates and alkyl acrylates as well as acrylonitrile and styrene, also to calculate the distribution of the organotin monomer in the copolymers showing azeotropic behaviour. It was also aimed to prepare terpolymers involving organotin monomers as well as acrylonitrile to illustrate the variation of both instantaneous and average terpolymer compositions with conversion on the basis of determined reactivity ratios. These values are expected to be very useful in selecting a suitable copolymer or terpolymer with a regular distribution of monomer units for obtaining optimum physical properties as well as increasing its biocidal efficiency.

The ultimate aim of this work which will be continued further to the present work is to reach such copolymer and terpolymer compositions which satisfy all practical requirements of molecular weight, application viscosity, uniform distribution of the toxic constituent, stability upon storage and longterm effective functioning in the desired application.

MATERIALS AND METHODS

CHAPTER II

MATERIALS AND METHODS

A- Materials

Acrylate and methacrylate monomers, namely, methyl methacrylate (MMA), allyl methacrylate (AMA), methyl acrylate (MA), ethyl acrylate (EA), and n-butyl acrylate (BA) were E. Marck Darmstadt, products and were freed from inhibitors by distillation under reduced pressure and the centre cuts were retained for use. Acrylonitrile (AN) and styrene (St) monomers were also purified by vacuum distillation.

The bis(tri-n-butyltin) oxide (TBTO) was obtained from M & T Chemicals, Rahway, New Jersey, and the free radical initiator, azo-bis-isobutyronitrile (AIBN) from Eastman Kodak co., was recrystallized from absolute ethanol, m.p. 102°C.

All solvents used were of reagent grade and were purified by distillation before use.

B- Methods

1. Preparation of n-butyl methacrylate (BMA)

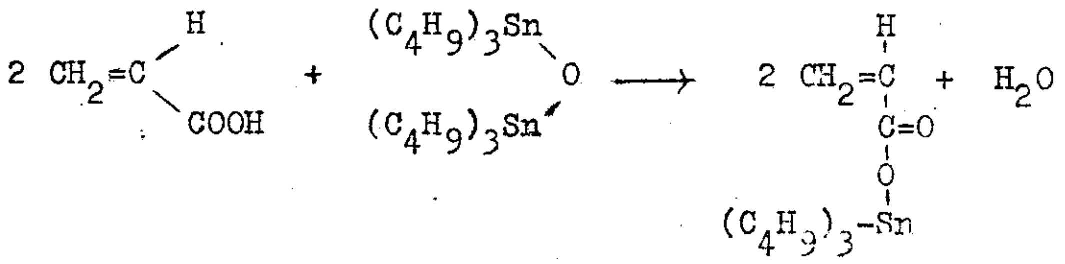
n-Butyl methacrylate monomer was prepared according to the method of Munch-Petersen[51] through esterification of methacrylic acid with n-butyl alcohol. Thus, to a solution of methacrylic acid (258 gm, 3 moles) in 300 ml benzene, in a 1 L flask, butanol (370 gm, 5 moles) was added and about 8 ml concentrated sulphuric acid was added dropwise to the reaction mixture. Also, 10 gm of hydroquinone was added to the reaction mixture as inhibitor. The flask was placed over a boiling water bath and provided with an azeotropic separator connected to a reflux condenser. The reaction mixture was heated under reflux for about 6 hours or until no separation of aqueous phase occurred. The cooled reaction mixture was diluted with 200 ml ether, washed with dilute sodium bicarbonate solution until neutral to litmus and dried over anhydrous sodium sulphate. The solvent was distilled off and the n-butyl methacrylate ester was purified from excess butanol by fractional distillation, b.p. 160°C.

2. Preparation of n-propyl methacrylate (PrMA)

n-Propyl methacrylate monomer was prepared according to Munch-Petersen[51] using the same procedure described before, based on the esterification of methacrylic acid with n-propyl alcohol. The prepared n-propyl methacrylate monomer was purified by fractional distillation, b.p. 140°C.

3. Preparation of tri-n-butyltin acrylate (TBTA)

The tri-n-butyltin acrylate monomer was prepared according to a modified method by Cummins and Dunn[52], based on the esterification of acrylic acid with tri-n-butyltin oxide as follows :

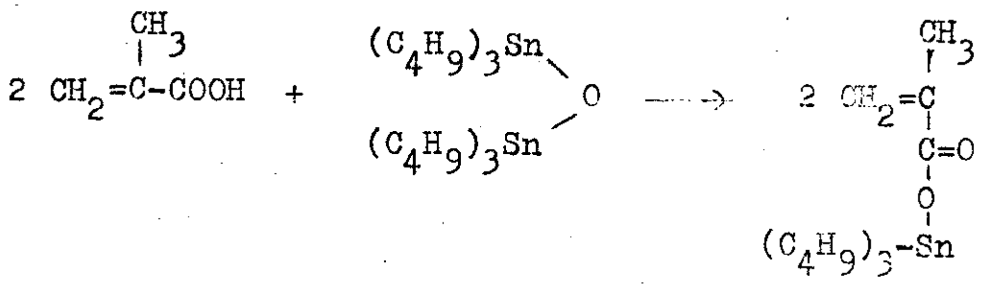


$$2\ CH_2{=}C\begin{smallmatrix}H\\ COOH\end{smallmatrix} + \begin{smallmatrix}(C_4H_9)_3Sn\\ (C_4H_9)_3Sn\end{smallmatrix}{>}O \longrightarrow 2\ CH_2{=}C(H)\!-\!C({=}O)\!-\!O\!-\!Sn(C_4H_9)_3 + H_2O$$

Thus, tri-n-butyltin oxide (100 gm, 0.167 mole) was added to 300 ml light petroleum in a 500 ml conical flask and the solution was stirred with a magnetic stirrer. Acrylic acid (24.16 gm, 0.335 mole) was added very slowly in a period of 2 hours at room temperature. After all the acid was added the reaction mixture was dried over anhydrous sodium sulphate and filtered. The resulting solution was left overnight in a refrigerator and the tri-n-butyltin acrylate monomer separated out as colourless needlelike crystals; it was collected by filtration and purified by recrystallization from petroleum ether, m.p. 75°C. The tin content of the monomer was found to be 32.71 % against a calculated value of 32.96 %. The yield was almost quantitative.

4. Preparation of tri-n-butyltin methacrylate (TBTMA)

The tri-n-butyltin methacrylate monomer was prepared according to a modified method by Cummins and Dunn[52], through the esterification of methacrylic acid with tri-n-butyltin oxide as follows :



Thus, tri-n-butyltin oxide (100 gm, 0.167 mole) was added to 300 ml light petroleum in a flask equiped with a mechanical stirrer. Then, methacrylic acid (28.8 gm, 0.335 mole) was added slowly to the solution while cooling down the flask to maintain the reaction mixture temperature below 30°C. All the acid was added dropwise in a period of 2 hours and the reaction mixture was left overnight in a refrigerator. The reaction mixture was poured over dilute sodium bicarbonate solution, washed with water in a separating funnel and the organic layer was collected and dried over anhydrous sodium sulphate, then filtered. The resulting solution was left overnight at -15°C to produce tri-n-butyltin methacrylate as colourless needles; it was collected by decantation of the supernatent liquid. The product was recrystallized from light petroleum at -15°C, and excess of the solvent was removed by vacuum evaporation. The tri-n-butyltin methacrylate monomer produced melted at 18°C, and its tin content was found to be 31.30 % against a calculated value of 31.73 %. The yield was almost quantitative.

5. Polymerization of tri-n-butyltin acrylate

Polymerization of tri-n-butyltin acrylate was carried out by solution polymerization in toluene to study the effect of both monomer and initiator concentration on the rate of polymerization. Thus, the required amounts of the tin monomer in toluene (0.77-1.61 mole/l) were charged in pyrex glass tubes. Azo-bis-isobutyronitrile was used as a free radical initiator and the calculated amount (0.0077-0.031 mole/l) was added to each tube. The tubes were flushed with oxygen-free nitrogen, and each tube was capped with aluminium foil, and placed in a thermostatically controlled waterbath at 70°C. After polymerization for a given time (20-80 min.) the contents of each tube were poured on large amount of 85 % methanol-water mixture. The precipitated polymer was purified by washing several times with 90 % methanol solution, then each sample was dried till constant weight. The percent conversion of each sample was calculated as the weight of polymer produced with respect to the weight of monomer.

6. Binary copolymerization reactions

The copolymers were obtained by the solution polymerization method in presence of azo-bis-isobutyronitrile as a free-radical initiator. Thus, the pre-determined amounts of the comonomers were placed in a small glass tubes, and diluted with toluene so that the total monomer concentration was about 3 moles/litre. The copolymerization was commenced by adding AIBN in a concentration of 1 mole/100 moles monomers to each tube. The tubes were flushed with oxygen-free nitrogen for 10 minutes, capped and thermostated at 70°C for 15-60 minutes depending on the comonomer pair and the initial composition. The copolymers were obtained by precipitation from 85 % methanol-water mixture, and purified by reprecipitation by 90 % methanol, and washing several times, dried and weighed. Conversions were limited within 7-10 %, since the calculations of the monomer reactivity ratios depend on the differential form of the copolymer composition equation. The percent conversion of each sample was evaluated as the weight of the copolymer produced with respect to the total weight of comonomers.

7. Ternary copolymerization reactions

Polymerization of the three component systems were carried out by solution polymerization using toluene as a solvent in presence of AIBN as a free radical initiator at 70°C according to the method described before for binary copolymerization reactions.

8. Determination of tin content

The tin content of the prepared monomers, copolymers and terpolymers was determined through oxidation of the sample to tin oxide according to the method of Gilman and Rosenberg[53]. Thus, approximately 0.2 gm of the tin-containing sample was placed in a 30 ml crucible. To this were added, with caution, 3 ml of concentrated sulfuric acid and 3-5 drops of nitric acid. The crucible was heated slowly over a flame until the sample turned black, and then cautious heating was maintained until the excess acid was removed. Subsequently, the carbonaceous material formed by the action of the acid was completely calcined for 1 hr over high heat, leaving the stannic oxide as a pale yellow solid residue. From the weight of this residue, the tin content of the sample was calculated as follows :

$$\text{Sn }\% = \frac{\text{weight of tin oxide} \times 119 \times 100}{\text{weight of sample} \times 151}$$

9. Determination of nitrogen content

The nitrogen content of the prepared ternary copolymers containing AN, was determined according to a modified micro-Kjeldahl procedure. Thus, about 0.3 gm of the sample was digested with concentrated sulphuric acid in presence of hydrogen peroxide. A solution of 50 % sodium hydroxide was added to the sample solution in the Kjeldahl apparatus and the ammonia was distilled and collected in boric acid solution. The nitrogen content of each sample was calculated by titration against a standard hydrochloric acid solution (0.01N) using mixed indicator of bromocresol and methyl red.

10. Viscosity measurements

A 1 % solution of each sample of the purified and dried polymers in toluene was prepared for viscosity measurements using Ubbelohde viscometer, in thermostatically controlled water bath at 30°C. The efflux time of the solvent was of the order of 180 seconds. The specific viscosity of each sample was calculated as :

$$\eta_{Sp} = \frac{t - t_o}{t_o}$$

where t and t_o are the efflux time of the polymer solution and the pure solvent, respectively.

11. Infrared spectroscopy

The prepared organotin monomers, copolymers and terpolymers were examined by infrared spectrophotometry using the thin-film technique on Beckman 4220 infrared spectrophotometer.

12. Determination of the monomer reactivity ratios

The monomer reactivity ratios of the binary copolymerization systems involving organotin monomers were determined on the basis of the comonomer composition-copolymer composition relationship. The copolymer composition of each sample was calculated through its tin content as follows :

$$\frac{\text{Sn \% of copolymer}}{\text{Sn \% of } M_1} = \frac{\text{mol. wt. of } M_1}{\text{mol. wt. of } M_1 + \text{mol. wt. of } M_2/b}$$

where M_1 is the organotin monomer and b (= m_1/m_2) is the molar ratio of copolymer composition, the molar fraction of M_1 monomer (F_1) in the copolymer could be calculated as :

$$F_1 = \frac{b}{1+b}$$

The monomer reactivity ratios of each system was calculated according to the method of Fineman-Ross[14] (page 20) and also by the method recently proposed by Kelen and Tüdős[18] (page 22).

13. Preparation and properties of Organotin Polymer Films

a- Preparation of Organotin Polymer Films

Films were made by pouring the solution of organotin polymer (50 % in toluene) on the clean dry glass and metal plates. Each run was performed in duplicate or triplicate. The plates were left to dry in suitable supports near the vertical position for two days at room temperature.

b- Determination of the Dry Film Thickness

An Erichsen mechanical thickness gauge was used to determine the film thickness.

c- Determination of the Film Hardness[54]

The film hardness was measured at the abovestated thickness using the standard Konig pendulum. The time (in seconds) required to damp the oscillation from the initial outwards portion marked by 6° to half amplitude marked by 3° was taken as the hardness indication, the time for uncoated glass is 210 sec.

d- Impact Resistance[55]

The Gardner impact tester was used. The weight of steel impact rod is 1810 grams.

e- Determination of Water Resistance[56]

In the present work, the films were prepared on clean glass plates. The plates were immersed to half the length in 2 litre beakers containing distilled water for 24 hours at room temperature. In the case of hot water, the immersion period ranged from 15 minutes to several hours. The panels were gently dried and left for one hour after removal from water, and then examined from any defect.

f- Determination of Alkali Resistance[57]

The test panels were coated by the resin material to be tested and allowed to dry. The edges were coated by dipping in molten paraffin wax. The coated panels were then immersed in an aqueous solution containing 5 gm of sodium hydroxide or anhydrous sodium carbonate per 100 ml of water for 4 hours.

The panels were removed, washed and the immersed portion of the film was examined immediately after drying for one hour for any defects.

g- Acid Resistance[58]

The panels were prepared in the same way as in the test for alkali resistance and immersed to half the length in a solution containing 5 gm of sulphuric acid (Sp. Gr. 1.84) per 100 ml of water and allowed to stand for 24 hours at room temperature. The panels were then removed and washed thoroughly with cold water and allowed to dry in vertical position for 2 hours at room temperature and the immersed portion of the film was examined for any defects.

h- Cross-cut Adhesion Test[59]

A very simple method for estimating adhesion consists in making a series of parallel cuts through the film in one direction and a second series at right angles to the first. To make the test quantitative, eleven cuts 1/32 inch apart in each direction, forming 100 squares. The number of squares remain intact gives a measure of the adhesion.

Applying adhesive tape to the cross-cut area to aid in removal of loose film may be helpful.