THESIS

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POLYMERIZATION, COPOLYMERIZATION AND TERPOLYMERIZATION OF ORGANOTIN MONOMERS

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SUMMARY

In the present work, tri-n-butyltin acrylate (TBTA) and tri-n-butyltin methacrylate (TBTMA) were prepared to study their polymerization, copolymerization and terpolymerization reactions.

The effect of monomer and initiator concentration on the polymerization rate of TBTA were studied and showed that the order of the reaction with respect to monomer concentration is unity, while with respect to initiator concentration is half order.

Copolymerization reactions of TBTA and TBTMA with methyl acrylate, ethyl acrylate, n-butyl acrylate, methyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, allyl methacrylate, styrene and acrylonitrile were studied, and the monomer reactivity ratios were determined according to the Fineman-Ross and Kelen-Tüdős methods, as illustrated in the following Table:

System M_1-M_2	Fineman-Ross method		Kelen-Tüdős method	
	r_1	r_2	r_1	r_2
TBTMA-MA	1.747	0.644	1.730	0.649
TBTMA-EA	1.259	0.606	1.262	0.613
TBTMA-BA	0.846	0.572	0.855	0.578
TBTMA-MMA	0.789	1.004	0.790	1.023
TBTMA-PrMA	0.580	0.900	0.571	0.893
TBTMA-BMA	0.623	0.646	0.642	0.678
TBTMA-AMA	2.306	1.013	2.380	1.058
TBTMA-St	0.256	1.104	0.259	1.108
TBTMA-AN	0.465	0.467	0.471	0.474
TBTA-MMA	0.401	2.199	0.395	2.180
TBTA-PrMA	0.323	1.713	0.314	1.684
TBTA-BMA	0.196	1.661	0.197	1.668
TBTA-AMA	0.195	2.575	0.201	2.619
TBTA-St	0.213	1.910	0.219	1.939
TBTA-AN	0.243	1.008	0.240	0.997

The determined reactivity ratios indicate that most of the copolymers should have random distribution of the monomer units, while the copolymerization of TBTMA with AMA shows tendency towards block copolymerization behaviour. Copolymerization reactions of TBTMA with propyl methacrylate, n-butyl methacrylate, n-butyl acrylate and acrylonitrile was found to give azeotropic copolymers at 19.23:80.77, 48.43:51.57, 73.53:26.47 and 49.91:50.02 molar ratios respectively, while the studied copolymerization reactions of TBTA did not show any azeotropic behaviour.

The terpolymerization reactions of seven systems involving the prepared organotin monomers and acrylonitrile with some acrylic or methacrylic esters were investigated. The ternary copolymerization reactions were performed at low conversions for two different feed compositions for each system. It was found that the predicted terpolymer compositions are in good agreement with the experimental results obtained from tin and nitrogen analyses. Also the variation of both the instantaneous and the average terpolymer composition as a function of conversion were calculated and verified experimentally for the studied ternary systems, over a wide range of conversion.

The structure of the prepared organotin monomers, copolymers and terpolymers were investigated by infrared spectroscopy. The prepared copolymers and terpolymers were soluble, colourless, transparent and suitable for film formation. Thus, organotin monomers were implicated in eleven co- and ter-polymer compositions and their film properties were investigated on glass and metal plates.

Three new organotin terpolymers were prepared from polymerization of methyl methacrylate, tri-n-butyl methacrylate and n-butyl methacrylate in different molar ratios to produce terpolymers with various tin contents as 15, 19 and 24 % in order to study their antifouling performance in the local marine environment. These organotin polymers, when tested as unpigmented and pigmented coatings in the eastern harbour of Alexandria, showed good antifouling efficiency which increased with increasing the tin content of the terpolymer. Some plates are now 15 months immersed in the sea in a testing raft and the plates are still free from fouling organisms.

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.

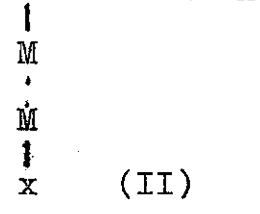
High polymers are composed of very large molecules, formed by linking together large numbers of simple chemical units (structural units). The structural units may be joined together in a variety of ways; in which simplest case the polymer may be represented by the formula (I) in which a simple, straight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

$$x \left[M \right]_n y$$

(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 :



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

(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.

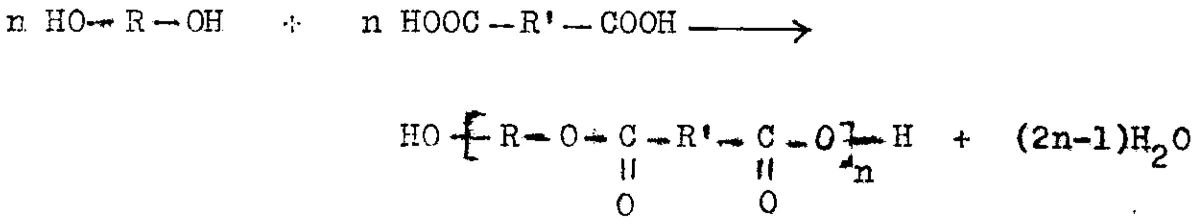
2. Classification of Polymers

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

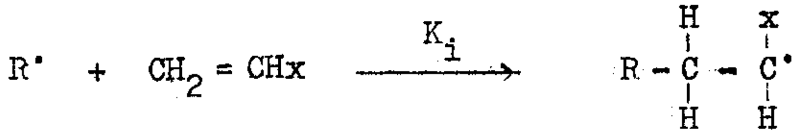
Free radical addition polymerization is a very powerful method for the preparation of polymers from a wide variety of unsaturated vinyl, vinylidene and diene monomers and is one of the most widely used industrial methods for the manufacture of addition polymers.

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:

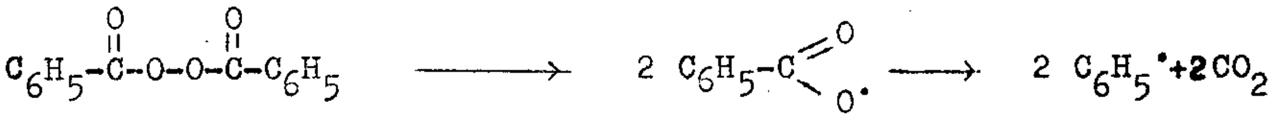


$$R^\bullet + CH_2 = CHx \xrightarrow{K_i} R-\overset{H}{\underset{H}{C}}-\overset{x}{\underset{H}{C}}{}^\bullet$$

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:



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2\ C_6H_5-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O^\bullet} \longrightarrow 2\ C_6H_5{}^\bullet + 2CO_2$$

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:

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

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:

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

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

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

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,

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

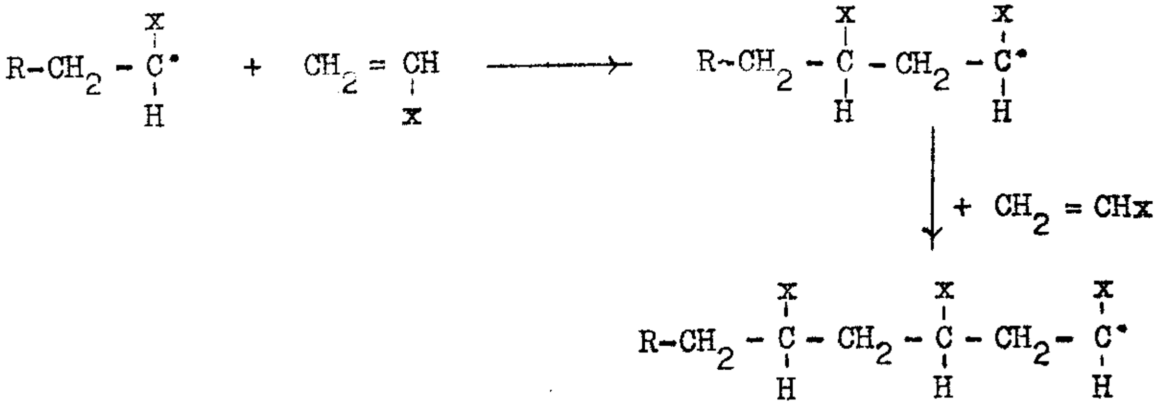
and bisulphite ions:

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

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:



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

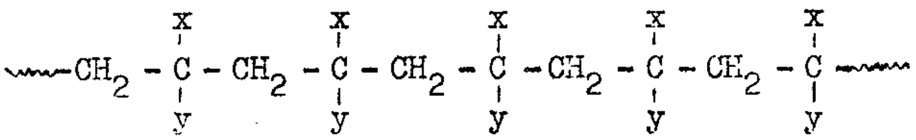
There are two possible points of attachment on monosubstituted (x = H) or 1-1-disubstituted monomers for a propagating radical either on carbon 1 or carbon 2 :

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

or

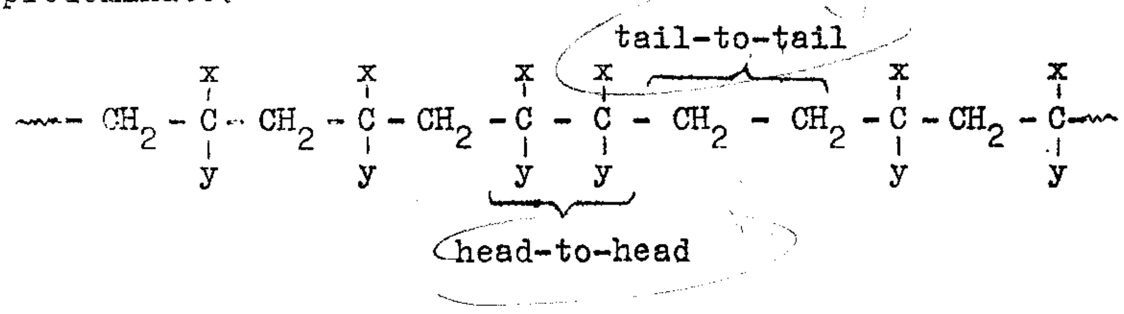
$$R^\bullet + \overset{x}{\underset{y}{C}}=CH_2 \longrightarrow R-CH_2-\overset{x}{\underset{y}{C}}{}^\bullet \qquad (2)$$

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.

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

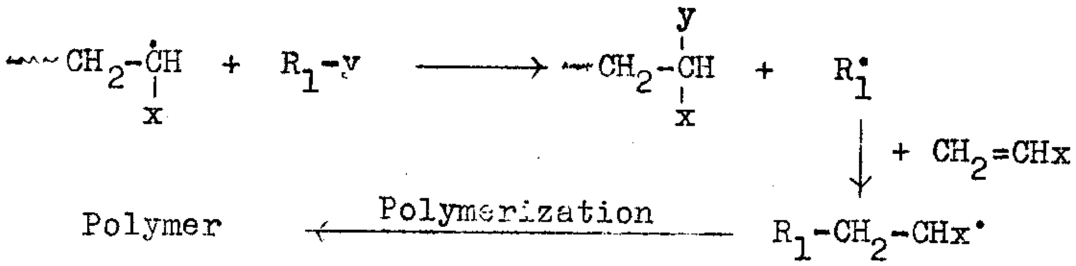
$$R\left[CH_2-CHx\right]_n CH_2-CH_2x + xHC{=}CH\left[CHx-CH_2\right]_m R$$

(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:



$$\begin{tikzcd}
\sim\sim CH_2-\underset{x}{\dot{C}H} + R_1-y \arrow[r] & \sim CH_2-\overset{y}{\underset{x}{CH}} + R_1^{\bullet} \arrow[d, "+\,CH_2=CHx"] \\
\text{Polymer} & R_1-CH_2-CHx^{\bullet} \arrow[l, "\text{Polymerization}"']
\end{tikzcd}$$

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:

$$\begin{array}{lll}
\left.\begin{array}{l}
\text{Initiator} \xrightarrow{K_D} 2\,R^{\bullet} \\
R^{\bullet} + M \xrightarrow{K_i} P_1^{\bullet}
\end{array}\right\} & \text{Initiation} \\
P_n^{\bullet} + M \xrightarrow{K_p} P_{n+1}^{\bullet} & \text{Propagation} \\
P_n^{\bullet} + P_m^{\bullet} \xrightarrow{K_t} \text{Polymer} & \text{Termination}
\end{array}$$

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 :

$$d\left[P^{\cdot}\right]/dt = I - K_t\left[P^{\cdot}\right]^2 = 0 \qquad (4)$$

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

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

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

$$-d\left[M\right]/dt = K_p/K_t^{1/2} \cdot \left[M\right] \cdot I^{1/2} \qquad (5)$$

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]:

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

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

$$\sim M_2^{\bullet} \quad + \quad M_2 \quad \xrightarrow{K_{22}} \quad \sim M_2M_2^{\bullet} \qquad (3)$$

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

where K_{11} is the rate constant for the reaction in which monomer M_1 adds to a radical chain ending in M_1, K_{12} is the rate constant for the reaction in which monomer M_2 adds to a radical chain ending in M_1 .... etc. 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 :

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

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

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 :

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

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 :

$$F_1 = f_1 = \frac{1-r_2}{2-r_1-r_2} \tag{13}$$

(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]

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

R. 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:

$$\begin{array}{lll}
M_1\text{-}M_2 & M_2\text{-}M_3 & M_1\text{-}M_3 \\
r_1 = K_{11}/K_{12} = r_{12} & r_1 = K_{22}/K_{23} = r_{23} & r_1 = K_{11}/K_{13} = r_{13} \\
r_2 = K_{22}/K_{21} = r_{21} & r_2 = K_{33}/K_{32} = r_{32} & r_2 = K_{33}/K_{31} = r_{31}
\end{array}$$

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:

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

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 :

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

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 :

$$d\,M_1 : d\,M_2 : d\,M_3 =$$

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

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.

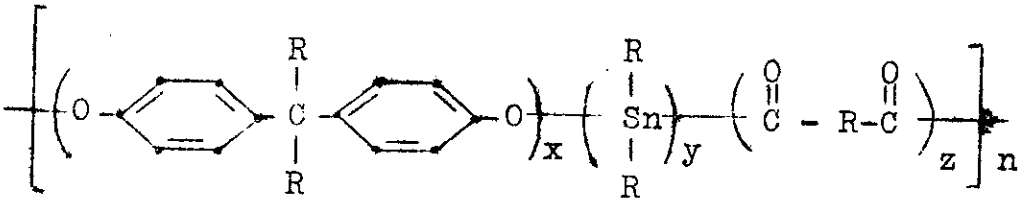
The literature dealing with organotin polymers is not extensive due to the secrecy which surrounds its most applications. Organotin polymers may be classified as substances containing tin atoms, bound to carbon, in the main chain or pendent in side chains.

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 :

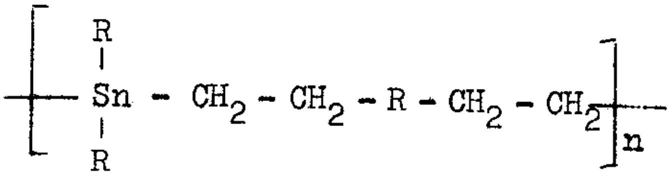
$$\mathrm{R_2SnCl_2} + \mathrm{R'(COONa)_2} \longrightarrow -\!\!\left[\mathrm{Sn(R_2)OOCR'COO}\right]_{n}\!\!- + \mathrm{2NaCl}$$

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 :



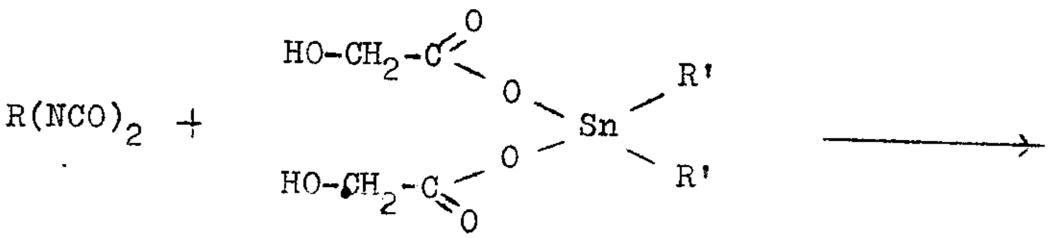
Noltes and Van der Kerk[32] studied the reactions involving organotin dihydrides and diolefins to prepare organotin polymers of the type :

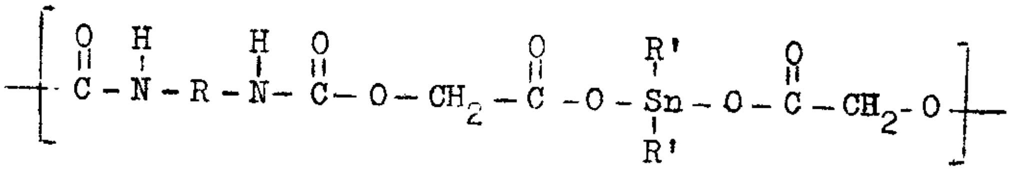
$$R_2SnH_2 \quad + \quad CH_2 = CH - R - CH = CH_2 \quad \longrightarrow$$



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

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 :





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

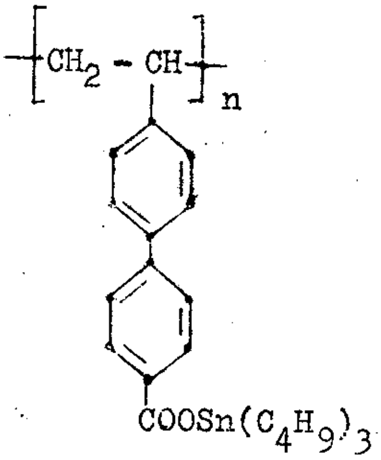
b) <u>Tin atoms pendent to polymer chain</u>

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 :

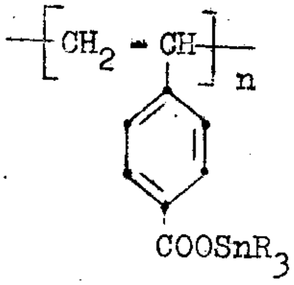
$$(R_3Sn)_2O \;+\; 2\; R'CH{=}CR''{-}COOH \longrightarrow 2\; R'CH{=}CR''COOSnR_3 \;+\; H_2O$$

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].

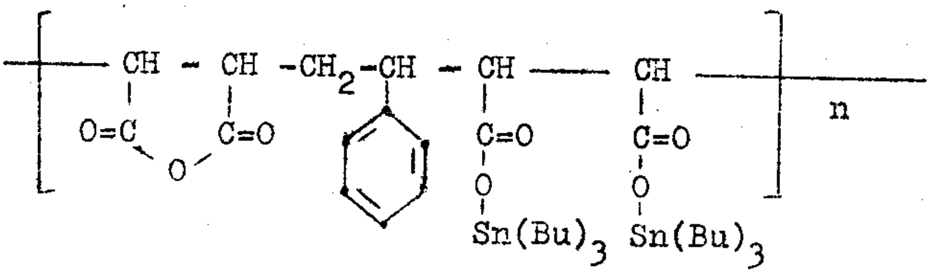
Adrova et al[36] prepared poly tributyltin-4'-vinyl-4-biphenyl carboxylate and reported it to be colourless soluble polymer, stable at 165°C, as :



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

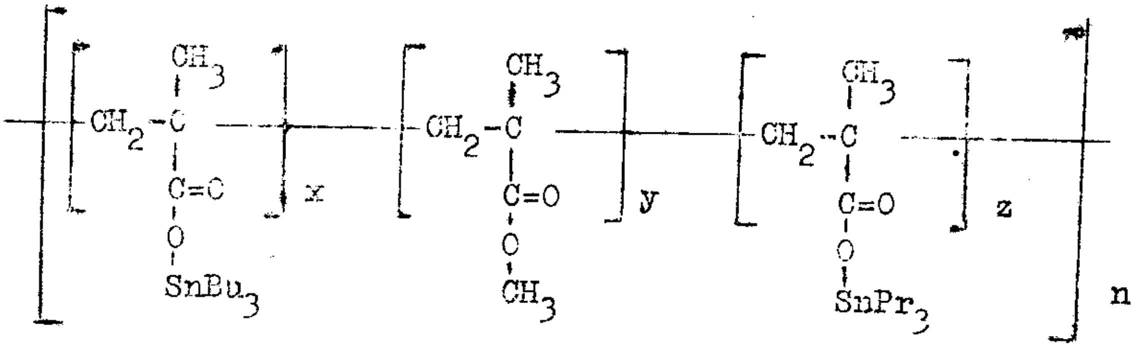


Kochkin[38] and Rzaev[39] studied a series of co- and terpolymers prepared from the reaction of maleic anhydride, styrene and organotin diester of maleic anhydride, with the following general structure :



These polymers were found to be resistant to 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 :



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)

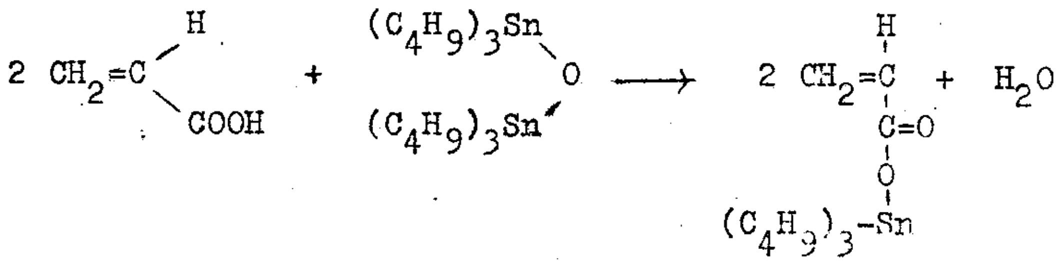
n-Butyl methacrylate monomer was prepared according to the method of Munch-Petersen[51] through esterification of methacrylic acid with n-butyl alcohol. Thus, to a solution of methacrylic acid (258 gm, 3 moles) in 300 ml benzene, in a 1 L flask, butanol (370 gm, 5 moles) was added and about 8 ml concentrated 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 :

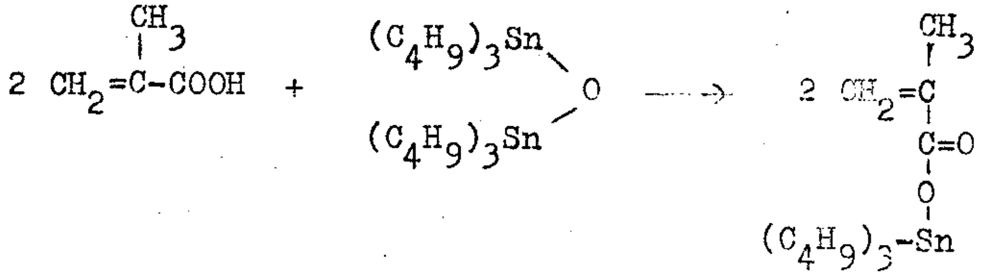


$$2\ CH_2{=}C(H)COOH + [(C_4H_9)_3Sn]_2O \longrightarrow 2\ CH_2{=}C(H){-}C({=}O){-}O{-}Sn(C_4H_9)_3 + H_2O$$

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 :



$$2\,CH_2{=}C(CH_3){-}COOH + \left[(C_4H_9)_3Sn\right]_2O \longrightarrow 2\,CH_2{=}C(CH_3){-}C({=}O){-}O{-}Sn(C_4H_9)_3$$

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.

RESULTS AND DISCUSSION

CHAPTER III

Polymerization Reactions

1. Tri-n-butyltin acrylate and tri-n-butyltin methacrylate monomers

The structure of the prepared tri-n-butyltin acrylate and tri-n-butyltin methacrylate monomers were investigated by their I.R. spectra as shown in Fig. (1). It can be shown that the I.R. spectra of the two tin-containing monomers are quite similar in the region 400-1400 cm^{-1} and are characterized by the presence of a strong band at 1640 cm^{-1} due to the carboxylate carbonyl groups of $-COOSn\lessgtr$. Cummins et al[52] reported that the tributyltin carboxylates exhibit only the 1640 cm^{-1} bands which are typical of a carbonyl rather than a carboxylate group due to the influence of the metal atom, which suggests that organotin esters are covalent and chelated in character rather than ionic compounds. The bands at 2970 cm^{-1} are due to the C-H stretching vibrations of $-CH_2$ and $-CH_3$ groups.

2. Polymerization of tri-n-butyltin acrylate (TBTA)

The polymerization of TBTA initiated by AIBN was carried out in toluene at 70°C. Two series of rate studies of the polymerization of TBTA were carried out in which the initial concentration of AIBN and that of TBTA was varied, while the other was maintained effectively constant, as follows :-

a) Effect of AIBN concentration on the rate of TBTA polymerization

To study the effect of the initiator concentration on the rate of TBTA polymerization, four polymerization reactions were carried out in which the concentration of TBTA was kept constant at 0.7777 mole/l and the AIBN at concentrations varying over 0.0077-0.0311 mole/l. The reaction conditions and results are summarized in Table (1). The time-conversion curves of the four polymerization reactions studied are shown in Fig. (2a), from which the rate of polymerization at each level of initiator concentration was calculated (Table 1).

B) Effect of monomer concentration on the polymerization rate of TBTA

Three polymerization reactions were carried out in which the AIBN concentration was kept at 0.0077 mole/l and the monomer concentration was varied over 0.7777-1.6163 mole/l. The results and experimental conditions are illustrated in Table (2). The time-conversion curves of the polymerization reactions studied are shown in Fig. (3a).

The relation between the rate of the reaction (R_p) as a function of initiator concentration (I), is illustrated logarithmically in Fig. (2b), from which the slope of the obtained straight line is equal to 0.5. This indicates that the order of the reaction with respect to the initiator concentration is a half-order reaction. Also, from Fig. (3b), it is clear that the order of reaction with respect to monomer concentration is equal to one. Accordingly, the rate equation for the radical polymerization of TBTA in toluene at 70°C, using AIBN as initiator could be obtained in the form of ideal polymerization behaviour as follows :

$$R_p = K \left[\mathrm{TBTA}\right]\left[\mathrm{AIBN}\right]^{1/2}$$

Deb and Samui[60] studied the kinetics of the polymerization of tri-n-butyltin methacrylate and reported that the polymerization showed deviations from ideal behaviour in that the initiator exponent fell below 0.5 at higher initiator concentrations, which may be due to the high viscosity of the monomer.

Table (1)

Effect of AIBN concentration on the rate of polymerization of TBTA (0.7777 mole/l, in toluene, at 70°C).

[AIBN] mole/l	Time min.	Conversion %	$\ln(R_p x10^5)$	$\ln([AIBN]x10^3)$
0.0077	20	9.2	1.7889	2.0412
	40	17.00		
	60	28.1		
	80	35.94		
0.0155	15	10.0	2.1456	2.7408
	20	12.5		
	30	20.0		
	40	26.0		
	50	33.0		
0.0226	10	8.5	2.408	3.1179
	18	16.0		
	28	24.1		
	40	32.5		
0.0311	8	8.5	2.5688	3.4372
	15	14.5		
	20	21.2		
	30	29.5		

Table (2)

Effect of monomer concentration on the rate of polymerization of TBTA (in toluene, at 70°C, in presence of 0.0077 mole/l AIBN)

[TBTA] mole/l	Time min.	Conversion %	ln(R_px10^5)	ln([TBTA]x 10)
0.7777	20	9.2	1.7889	2.0412
	40	17.0		
	60	28.1		
	80	35.94		
1.2725	27	13.11	2.3448	2.5436
	47	23.08		
	62	30.6		
	77	38.13		
1.6163	25	13.98	2.6966	2.7827
	45	24.37		
	60	32.53		
	75	40.23		

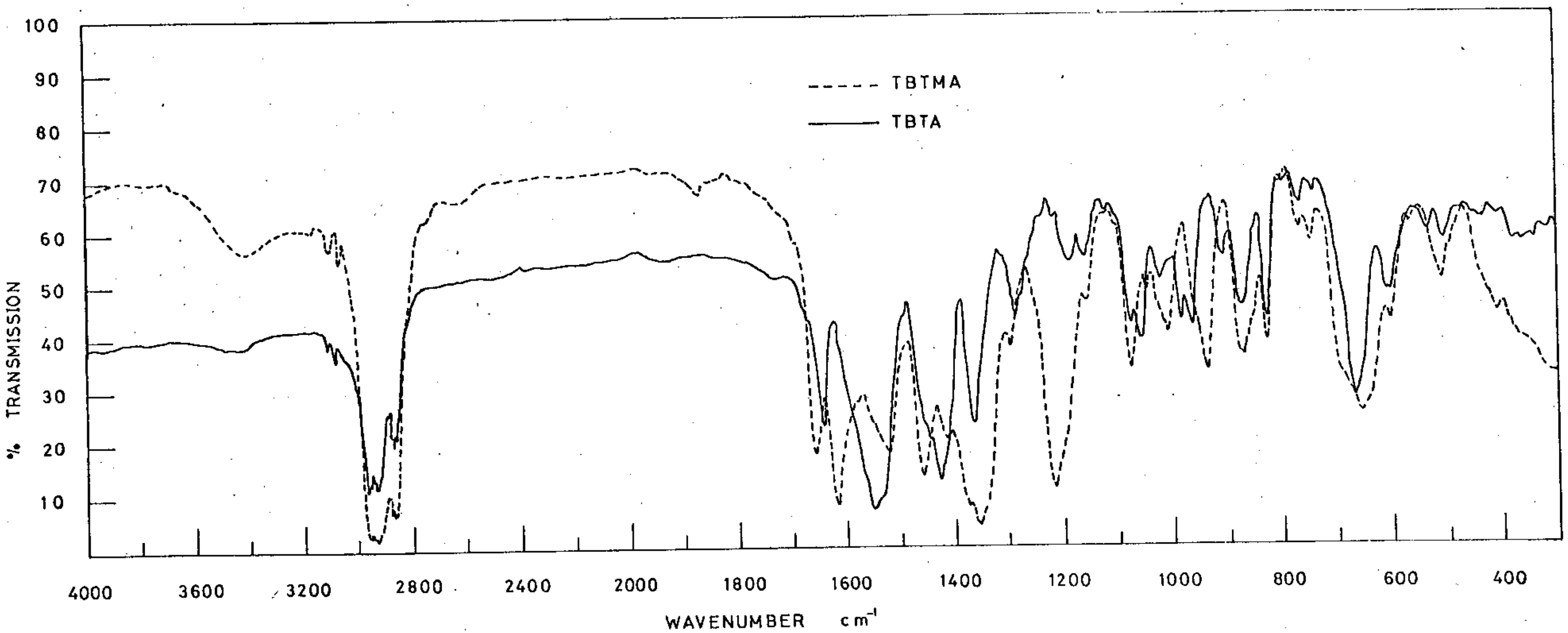


Fig. (1). The infrared spectra of TBTMA, and TBTA.

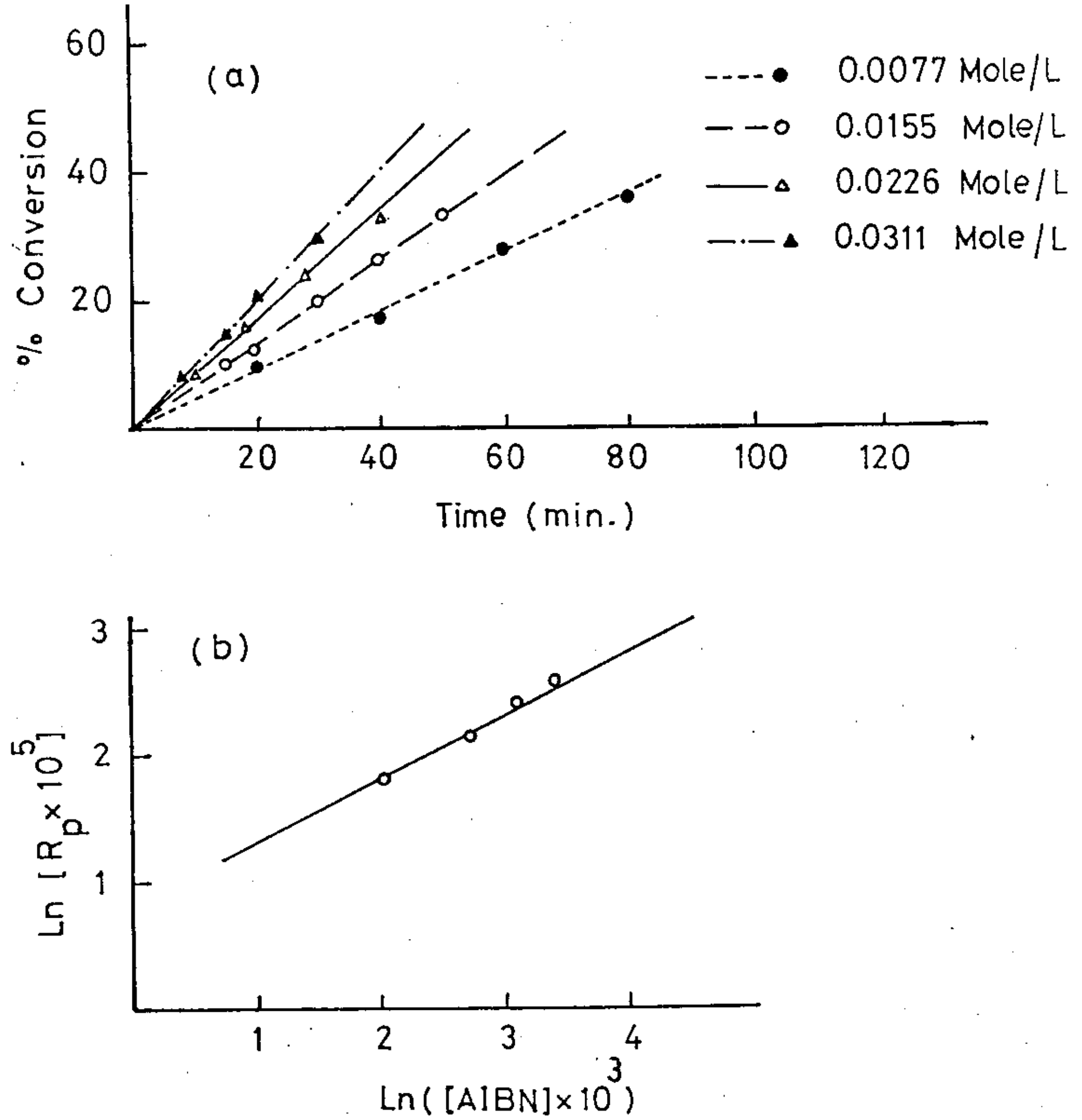
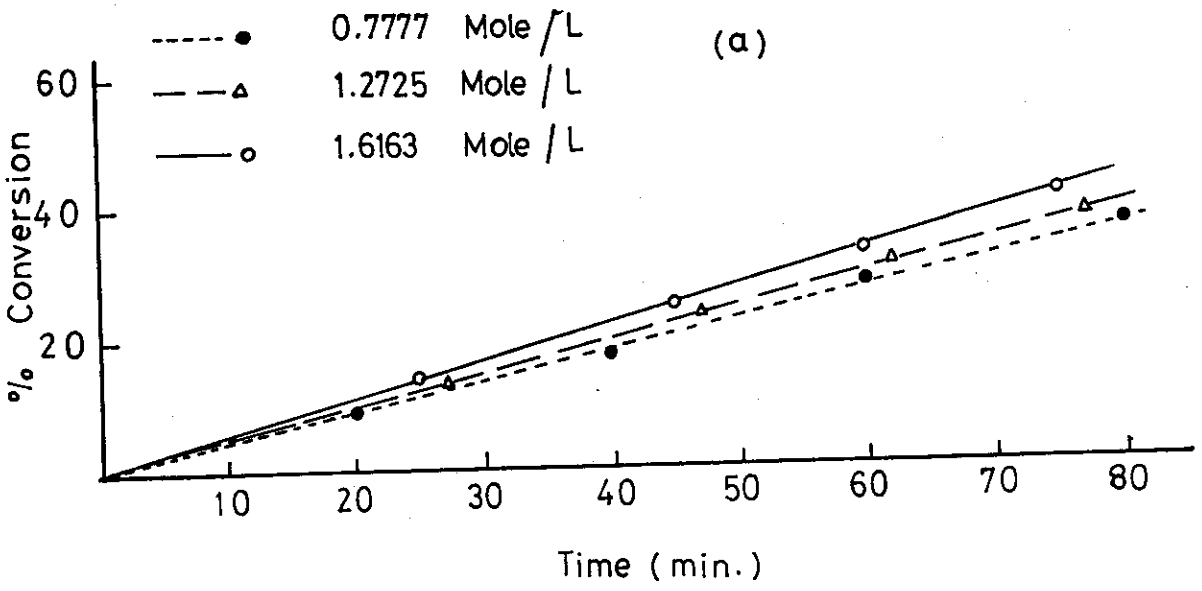


Fig. (2). Effect of AIBN concentration on the R_p of TBTA.



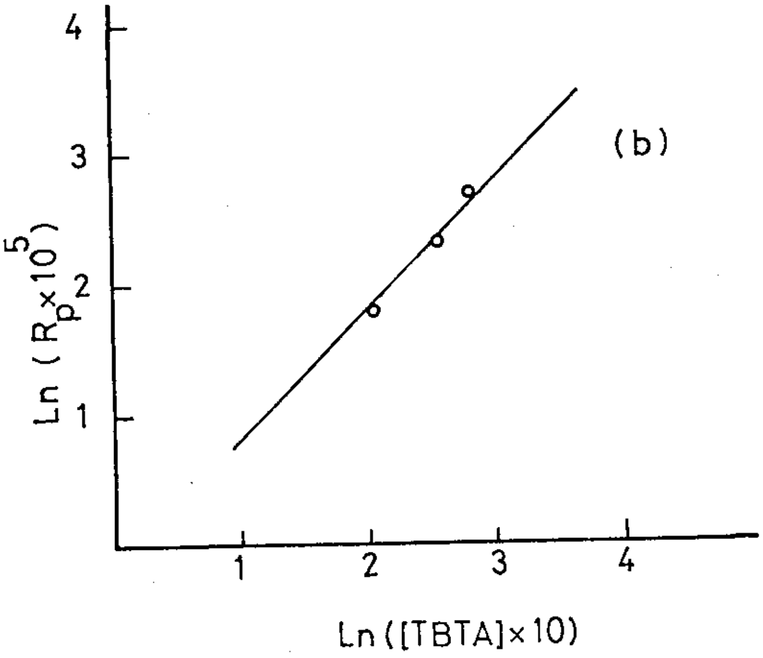


Fig. (3). Effect of TBTA concentration on its rate of polymerization.

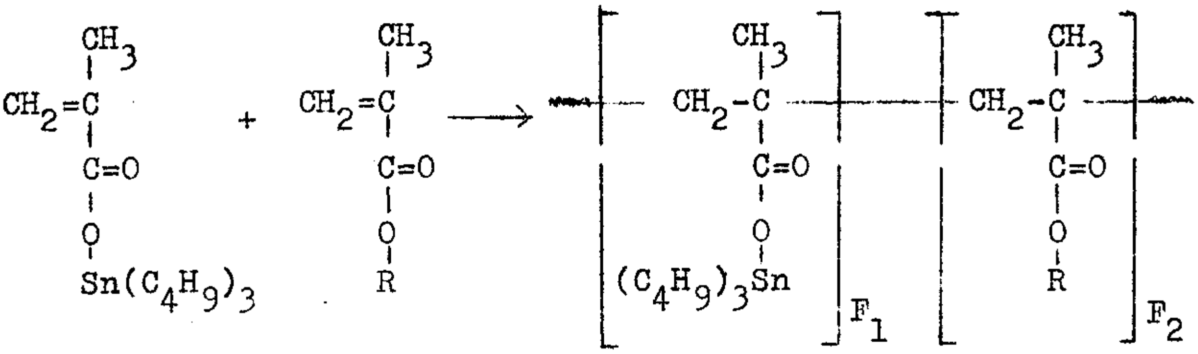
CHAPTER IV

Copolymerization Reactions

The copolymerization reactions of tri-n-butyltin methacrylate or acrylate with methacrylate esters, acrylate esters, styrene or acrylonitrile, were carried out by solution polymerization in toluene at 70°C in presence of 1 mole % AIBN as described earlier (page 45). The copolymers were prepared at low conversions and the copolymer composition of each sample was calculated from its tin content. The monomer reactivity ratios (r_1 and r_2) of each system were calculated according to Fineman and Ross[14] (page 20) and also by the method recently developed by Kelen and Tüdős[18] (page 22).

Monomer reactivity ratios for copolymerizations of tri-n-butyltin methacrylate (TBTMA) with methyl methacrylate (MMA), n-propyl methacrylate (PrMA), n-butyl methacrylate (BMA) and allyl methacrylate (AMA).

The copolymerization reactions of TBTMA with MMA, PrMA, BMA and AMA were studied and the reactions can be represented as:



$$CH_2{=}C(CH_3)COOSn(C_4H_9)_3 + CH_2{=}C(CH_3)COOR \longrightarrow -[CH_2-C(CH_3)(COOSn(C_4H_9)_3)]_{F_1}-[CH_2-C(CH_3)(COOR)]_{F_2}-$$

where R = $-CH_3$, $n-C_3H_7$, $n-C_4H_9$ or $-CH_2-CH=CH_2$.

The experimental conditions and the results of the copolymerization reactions are illustrated in Tables (3-6).

Fig. (4) shows the Fineman-Ross plots of a-a/b as a function of a^2/b for the copolymerizations of TBTMA with MMA, PrMA, BMA, and AMA. The slope of the straight line of each system is equal to r_1 and the intercept gives $-r_2$. Also, Fig. (5) illustrates the Kelen-Tüdős plots of the four systems which give r_1 and $-r_2/\alpha$ both as intercepts.

From the experimental data tabulated in Tables (3-6) and figures (4 and 5) for the copolymerization of the four systems studied, the monomer reactivity ratios calculated by both Fineman-Ross and Kelen-Tüdős methods are summarized in Table (7). The data illustrated in Table (7) show that there is a good agreement between the monomer reactivity ratios calculated by the two methods. Also, the range of experimental error in r_1 and r_2 is quite small and can be considered as within the experimental error.

From the reactivity ratios of the four systems studied and tabulated in Table (7), it is clear that the copolymer should have random distribution of the monomer units in the copolymer molecules. The copolymerization of TBTMA with MMA shows almost

Table (3)

Copolymerization of TBTMA (M_1) with MMA (M_2)

Initial monomer composition		Conversion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.9102$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ε
5.6445	0.8495	7.93	29.99	4.5944	0.8213	4.4160	6.9346	0.5629	0.8839
4.1867	0.8072	5.56	29.46	3.4601	0.7757	2.9768	5.0588	0.4981	0.8477
2.3467	0.7012	6.54	28.08	2.0138	0.6682	1.1814	2.5070	0.3241	0.5503
1.5165	0.6026	4.87	26.30	1.3091	0.5669	0.3581	1.7566	0.1343	0.6587
0.9882	0.4970	8.52	24.40	0.8908	0.4711	-0.1210	1.0961	-0.0604	0.5464
0.6893	0.4080	10.53	22.00	0.6085	0.3775	-0.4433	0.7807	-0.2623	0.4617
0.4303	0.3000	9.85	18.80	0.3897	0.2804	-0.6739	0.4753	-0.4864	0.3430
0.2527	0.2010	7.54	15.01	0.2393	0.1931	-0.8030	0.2668	-0.6824	0.2268
0.1834	0.1550	8.81	12.64	0.1767	0.1502	-0.8545	0.1903	-0.7766	0.1728
0.1139	0.1023	9.50	9.18	0.1086	0.0980	-0.9349	0.1194	-0.9079	0.1159

(*) Molar ratio (○) Mole fraction

Table (4)

Copolymerization of TBTMA (M_1) with PrMA (M_2)

Initial monomer composition		Conversion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 1.1989$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ε
5.6461	0.8494	7.22	29.11	3.7921	0.7913	4.1571	8.4065	0.4328	0.8752
3.9826	0.7995	9.63	28.08	2.6264	0.7245	2.4662	6.0389	0.3407	0.8344
2.9849	0.7490	11.72	27.29	2.0976	0.6779	1.5619	4.2477	0.2868	0.7799
2.3201	0.6989	10.35	26.53	1.7421	0.6353	0.9884	3.0899	0.2304	0.7205
1.4888	0.5980	4.86	24.24	1.1024	0.5243	0.1383	2.0106	0.0431	0.6265
0.9902	0.4977	3.99	22.22	0.7972	0.4435	-0.2518	1.2300	-0.1037	0.5064
0.6603	0.3977	7.17	19.72	0.5604	0.3591	-0.5179	0.7780	-0.2620	0.3935
0.4117	0.2916	7.46	17.13	0.4011	0.2861	-0.6145	0.4224	-0.3791	0.2606
0.2406	0.1939	8.19	13.41	0.2497	0.1998	-0.7226	0.2317	-0.5053	0.1621
0.1764	0.1510	3.04	11.03	0.1820	0.1540	-0.7931	0.1711	-0.5788	0.1247

(*) **Molar ratio** (°) **Mole fraction**

Table (5)

Copolymerization of TBTMA (M_1) with BMA (M_2)

Initial monomer composition		Conversion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.8024$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	γ	ε
4.8110	0.8279	7.84	28.64	3.5045	0.7780	3.4382	6.6045	0.4642	0.8917
3.3813	0.7717	5.62	27.63	2.5340	0.7170	2.0470	4.5118	0.3852	0.8490
2.8280	0.7387	6.76	27.21	2.3030	0.6973	1.6001	3.4720	0.3743	0.8123
2.2385	0.6912	8.53	26.71	2.0054	0.6672	1.1223	2.4980	0.3399	0.7569
1.8110	0.6443	7.54	25.57	1.5705	0.6109	0.6575	2.0880	0.2266	0.7224
1.1260	0.5296	4.51	23.55	1.0893	0.5213	0.0924	1.1638	0.0469	0.5919
0.8068	0.4460	9.07	21.40	0.7830	0.4391	-0.2235	0.8312	-0.1369	0.5038
0.5157	0.3402	7.04	19.07	0.5705	0.3630	-0.3890	0.4664	-0.3061	0.3674
0.2815	0.2196	6.56	15.75	0.3731	0.2717	-0.4729	0.2122	-0.4661	0.2092
0.1245	0.1107	7.52	9.44	0.1590	0.1373	-0.6585	0.0974	-0.7318	0.1083

(*) Molar ratio (∘) Mole fraction

Table (6)

Copolymerization of TBTMA (M_1) with AMA (M_2)

Initial monomer composition		Conversion %	Sn%	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.6255$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ξ
3.9129	0.7964	9.37	30.47	8.3333	0.8904	3.3434	1.8373	1.3981	0.7460
2.9068	0.7440	8.25	29.94	5.6529	0.8489	2.3926	1.4947	1.1285	0.7050
2.3723	0.7035	7.38	29.40	4.2391	0.8091	1.8127	1.3276	0.9281	0.6797
1.4763	0.5962	9.82	28.34	2.7724	0.7375	0.9438	0.7861	0.6685	0.5569
0.9727	0.4931	8.34	26.68	1.7835	0.6402	0.4273	0.5305	0.3697	0.4589
0.6585	0.3971	9.14	23.39	0.9423	0.4852	-0.0403	0.4602	-0.0371	0.4238
0.4256	0.2986	7.31	19.95	0.5690	0.3629	-0.3223	0.3183	-0.3416	0.3372
0.2528	0.2018	9.87	14.97	0.3001	0.2308	-0.5896	0.2129	-0.7032	0.2540

(*) Molar ratio (o) Mole fraction

Table (7)

Monomer reactivity ratios in copolymerization of TBTMA with MMA, PrMA, BMA and AMA

M_1 - M_2	Fineman-Ross method			Kelen-Tüdős method		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
TBTMA-MMA	0.789±0.012	1.004±0.034	0.792	0.790±0.010	1.023±0.009	0.808
TBTMA-PrMA	0.580±0.012	0.900±0.046	0.522	0.571±0.014	0.893±0.024	0.510
TBTMA-BMA	0.623±0.016	0.646±0.048	0.402	0.642±0.022	0.678±0.028	0.435
TBTMA-AMA	2.306±0.100	1.013±0.104	2.336	2.380±0.145	1.058±0.078	2.518

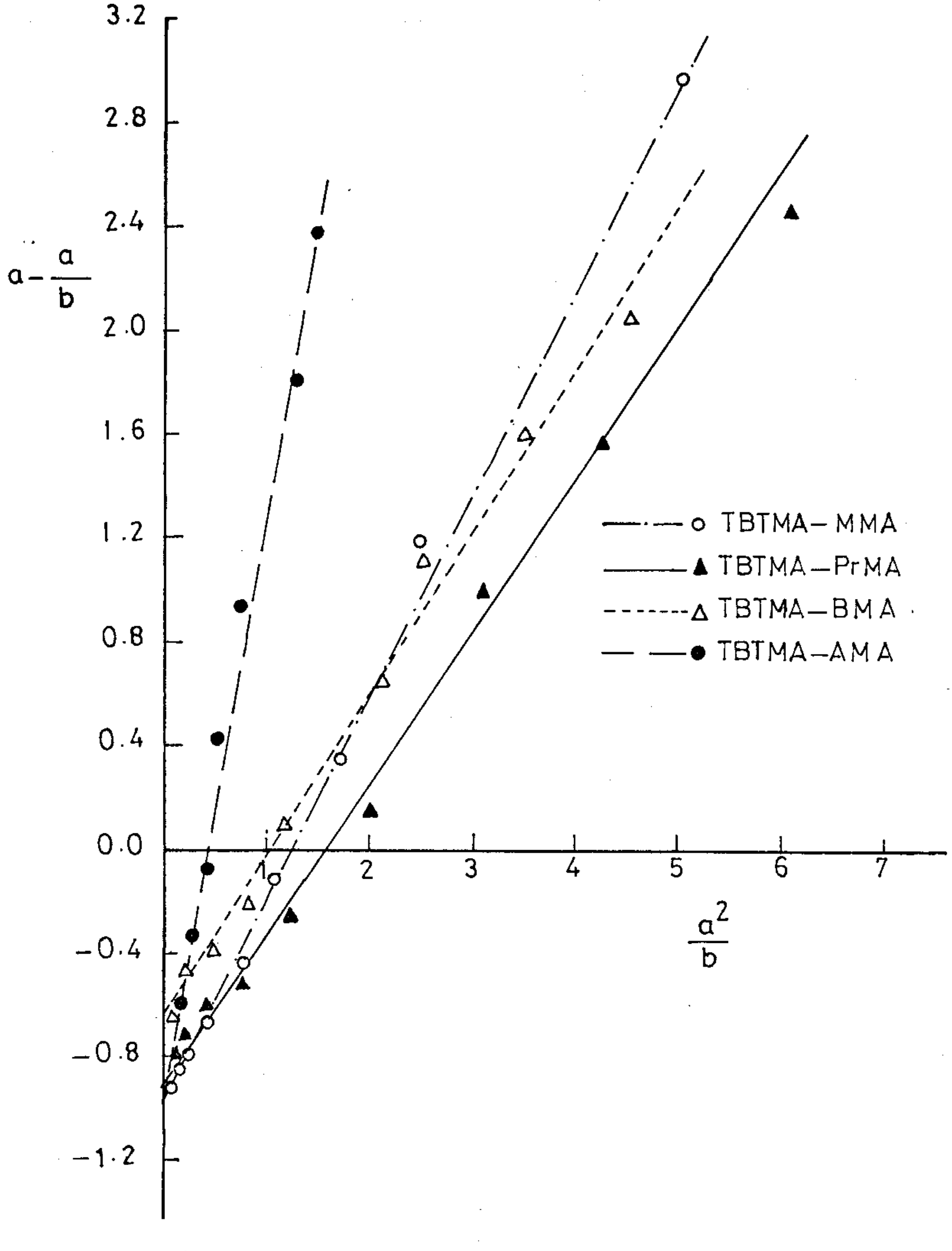


Fig. (4). Fineman–Ross plots for the copolymerization of: TBTMA–MMA, TBTMA–PrMA, TBTMA–BMA, and TBTMA–AMA.

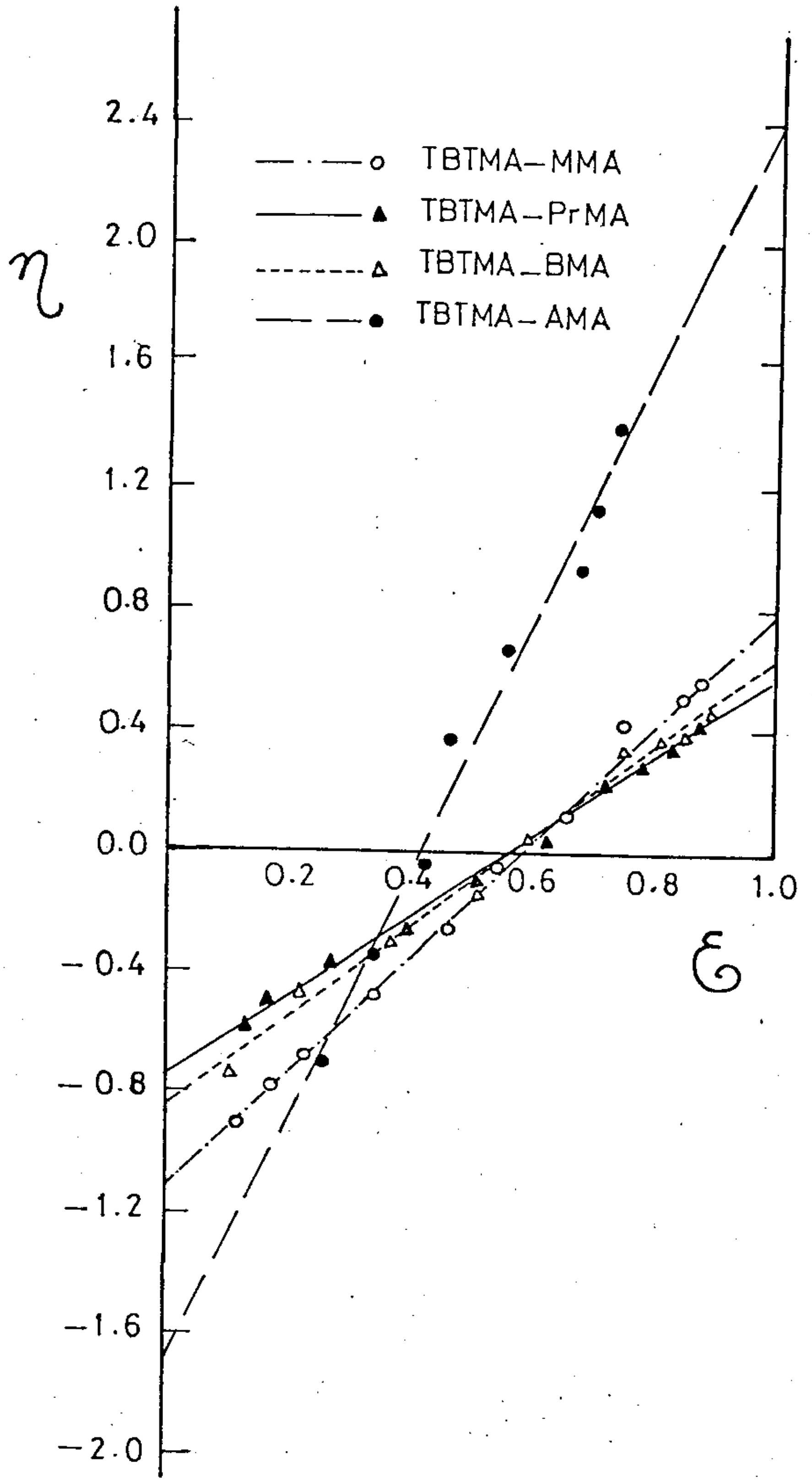


Fig. (5). Kelen–Tüdős plots for the copolymerization of: TBTMA–MMA, TBTMA–PrMA, TBTMA–BMA and TBTMA–AMA.

ideal behaviour (r_1r_2 = 0.792, while copolymerization of TBTMA with AMA shows almost block copolymerization behaviour ($r_1 > 1$, $r_2 > 1$ and r_1r_2 = 2.336). Table (7) also shows that the monomer reactivity ratios determined for the copolymerization of TBTMA with PrMA and BMA are less than unity and should have azeotropic copolymerization behaviour. The azeotropic composition of TBTMA-PrMA system was calculated from the monomer reactivity ratios and was found to be at 19.23 : 80.77 mole ratio. Similarly the azeotropic composition of TBTMA-BMA system was found to be 48.43 : 51.57 mole ratio. These data are in agreement with the composition curves shown in Fig. (6) illustrating the relation between F_1 (mole fraction of TBTMA in copolymer) versus f_1 (mole fraction of TBTMA in comonomer feed). From figures 6b and 6c it is clear that the curves cross the line representing $F_1 = f_1$ at 0.19 and at 0.48 mole fractions for copolymerizations of TBTMA with PrMA and BMA, respectively. These points of intersection correspond to the azeotropic compositions yielding homogeneous copolymers regardless of conversion.

The azeotrppic comonomer composition of TBTMA-PrMA and TBTMA-BMA systems were polymerized; by solution copolymerization in toluene in presence of 1 mole % AIBN at 70°C to several conversions covering a wide range. Tables 8 and 9 illustrate the experimental conditions and the results for both systems.

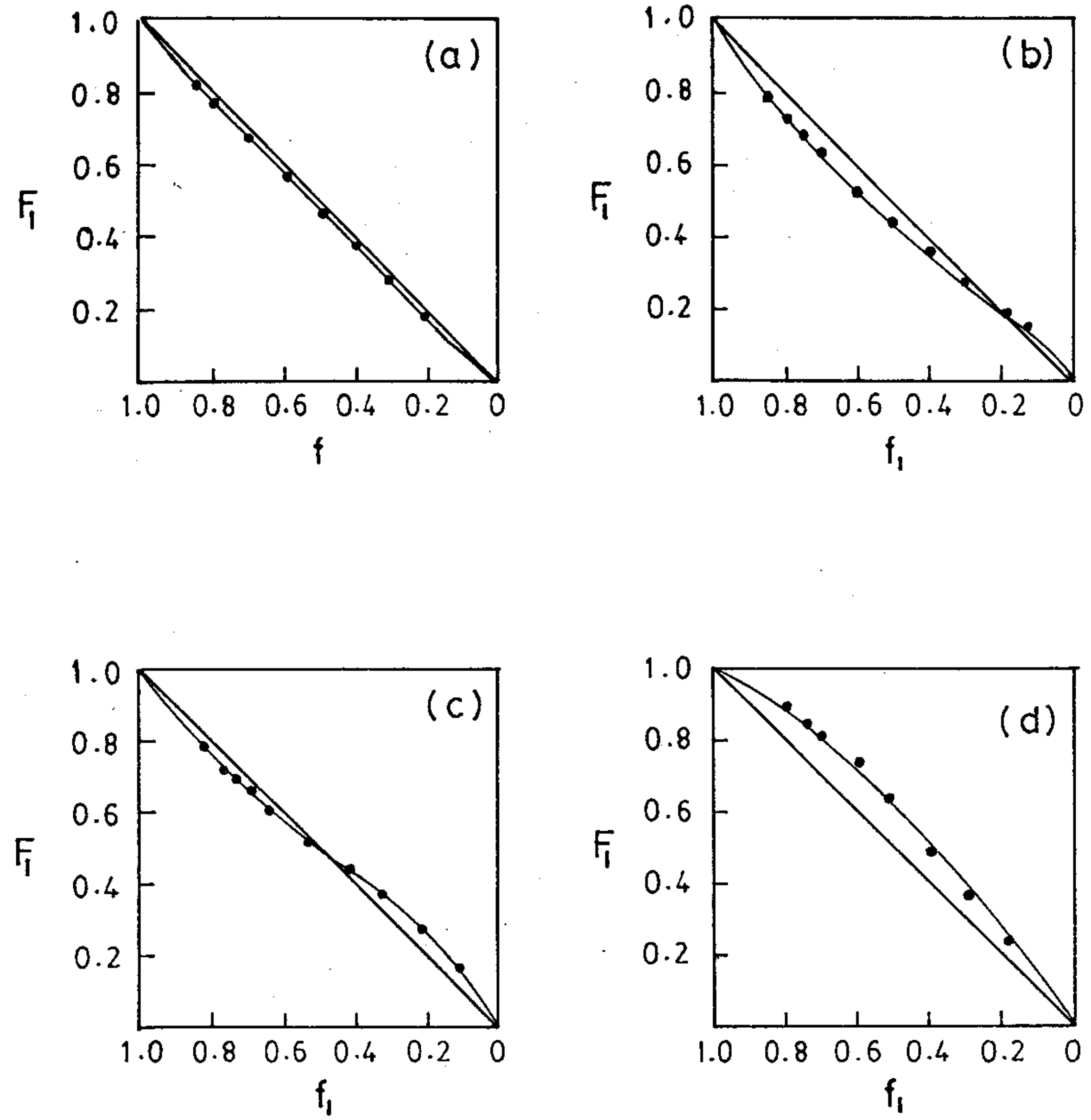


Fig. (6). Composition curves for the copolymerization of: (a) TBTMA–MMA, (b) TBTMA–PrMA, (c) TBTMA–BMA, and (d) TBTMA–AMA.

f_1 = mole fraction of M_1 in feed and

F_1 = mole fraction of M_1 in copolymer.

Fig. (7) shows the change of the conversion with time for both azeotropic copolymerizations. Fig. (8) shows F_1 (mole fraction of TBTMA in copolymer) against the conversion and that the experimental points - calculated from the tin content of each sample - are in good agreement with the points of inflection on the lines representing the azeotropic composition in both systems.

From Tables (8) and (9), and Fig. (8), it is clear that the azeotropic copolymer composition of TBTMA-PrMA and TBTMA-BMA systems remain constant up to 90 % conversion, and the tin content of the copolymers gave a mean value of 13.0 percent against a calculated value of 12.9 percent for the azeotropic composition of TBTMA-PrMA system, while for the azeotropic copolymerization of TBTMA with BMA gave a mean value of 22.62 % tin against a colculated value of 22.6 %.

Izu and O'Driscoll[61] proposed a normograph for calculating the sequence distribution of the monomers in the copolymer chain based on the feed composition and the monomer reactivity ratios. Thus, the triad fractions of TBTMA (M_1) for the azeotropic compositions of TBTMA-PrMA and TBTMA-BMA systems were calculated and found to be as follows :

Table (8)

Azeotropic copolymerization of TBTMA (M_1) with PrMA (M_2)

	mole fraction	gram
TBTMA :	0.192	10.8
PrMA :	0.808	15.51
AIBN :	(1 mole %)	0.246

Solution polymerization in toluene (3 moles/l, total volume 50 ml), at 70°C.

Time (minutes)	Conversion %	Sn %	F_1
40	14.75	13.02	0.1919
50	18.23	13.78	0.2076
60	27.01	13.62	0.2043
90	48.06	12.73	0.1861
120	61.82	12.77	0.1869
180	90.03	12.89	0.1893

Table (9)

Azeotropic copolymerization of TBTMA (M_1) with BMA (M_2)

	Mole fraction	Gram
TBTMA :	0.4843	27.24
BMA :	0.5157	10.984
AIBN :	(1 mole %)	0.246

Solution polymerization in toluene (3 moles/l, total volume 50 ml) at 70°C.

Time (minutes)	Conversion %	Sn %	F_1
90	4.37	22.42	0.4770
120	19.7	22.67	0.4865
150	26.83	22.39	0.4758
180	37.27	22.73	0.4889
200	42.24	22.84	0.4931
230	50.25	22.58	0.4831
290	75.13	22.86	0.4939
360	90.27	22.45	0.4781

	F_{111}	f_{112}	f_{121}	f_{212}
TBTMA - PrMA	0.0022	0.0179	0.0356	0.1502
TBTMA - BMA	0.0622	0.1105	0.1717	0.1928

which indicates that the alternating behaviour of TBTMA-BMA system is greater than that of TBTMA-PrMA system.

The structure of the prepared copolymers of tributyltin methacrylate with the alkyl esters of methacrylic acid as well as allyl methacrylate was investigated by infrared spectroscopy and were found to be quite similar in the region between 400 cm^{-1} to 1400 cm^{-1}. Also, the I.R. spectra of these copolymers are characterized by the presence of two strong bands at 1640 cm^{-1} and at 1730 cm^{-1} due to the stretching frequencies of the $>C=O$ groups of tributyltin carboxylates and the methacrylic esters, respectively. The bands at 2850-3000 cm^{-1} are due to the symmetrical and assymetrical stretching frequencies of the C-H bond due to $-CH_2$ and $-CH_3$ groups. Fig. (9) illustrates the I.R. spectrum of the TBTMA-AMA copolymer as an example of the studied copolymerizations of TBTMA with methacrylic acid esters.

Copolymers prepared from the reaction of TBTMA with alkyl methacrylates are clear, transparent and soluble in most organic solvents even at higher conversions, except methanol, while the copolymer of TBTMA with AMA gave an insoluble gel product at higher conversions. Also, copolymers produced from TBTMA with MMA were clear solids suitable for film formation while those from TPTMA with both PrMA and BMA were rubbery products and gave tacky films.

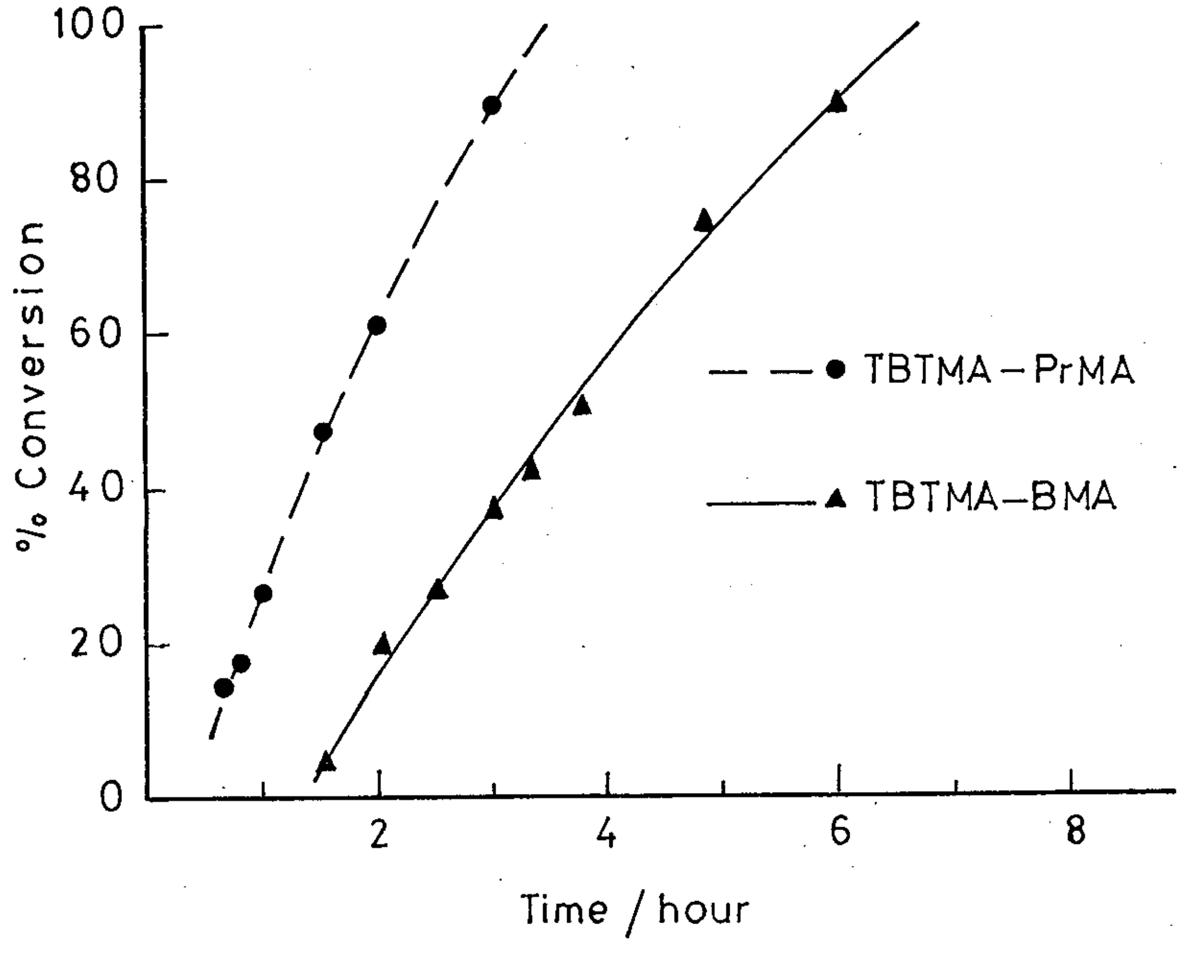


Fig. (7). Variation in percent azeotropic copolymers produced with time for: TBTMA–BMA and TBTMA–PrMA.

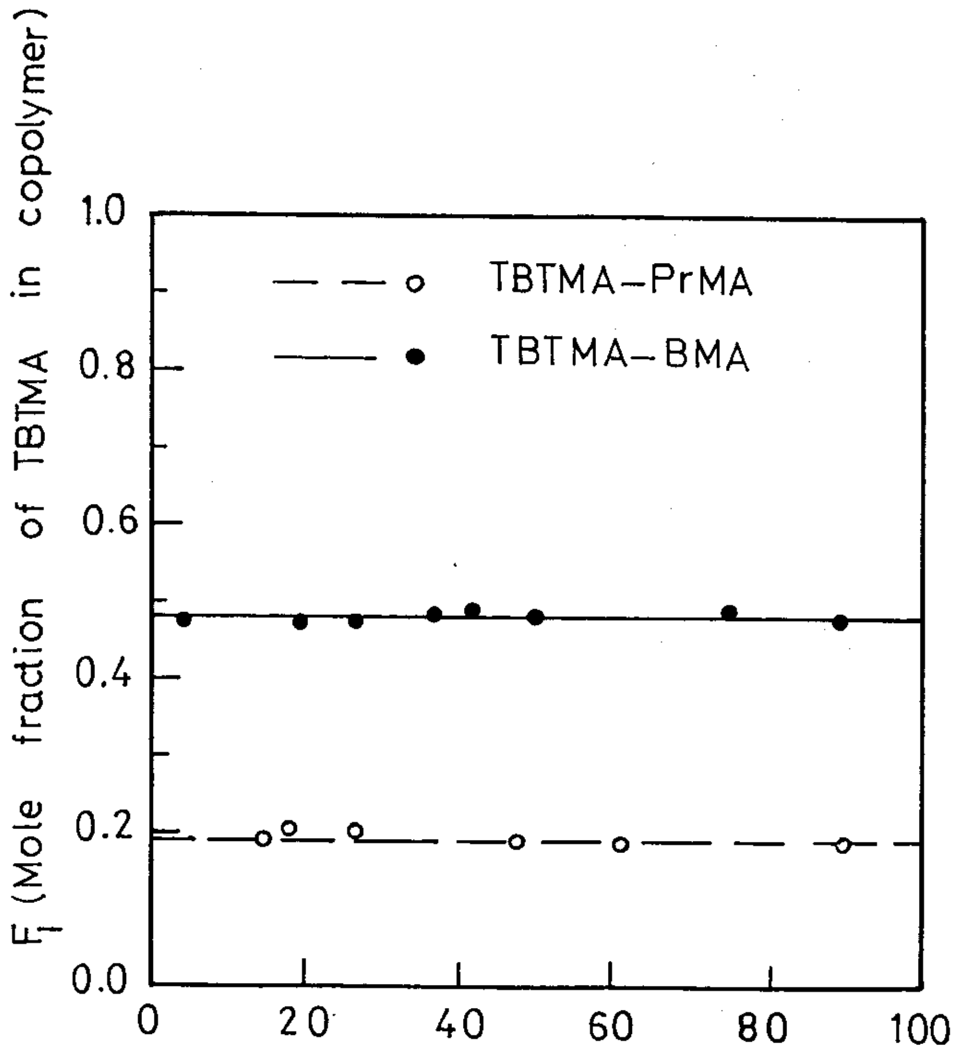


Fig. (8). F_1 as a function of conversion for azeotropic copolymerizations of : TBTMA–PrMA and TBTMA–BMA.

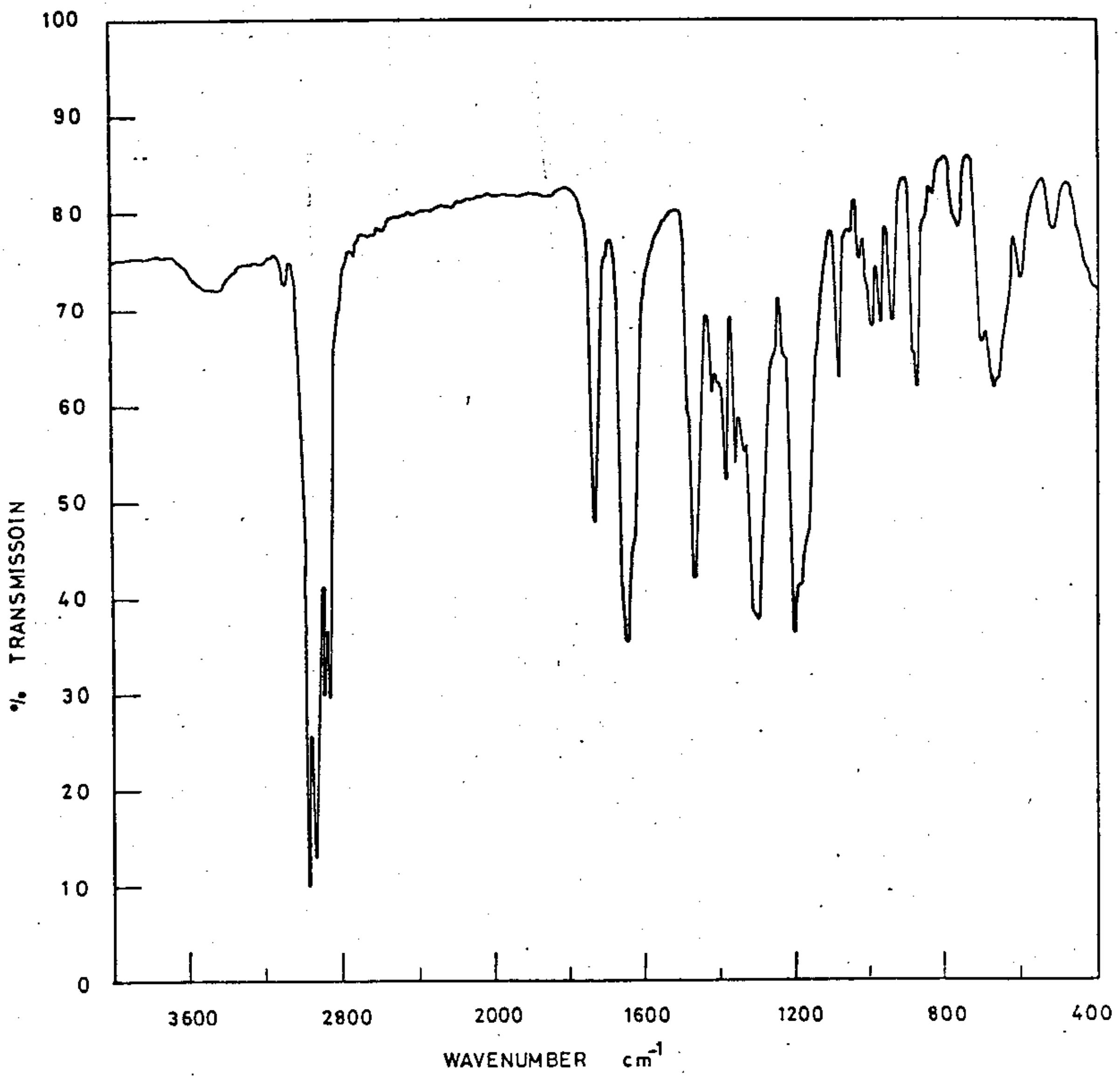
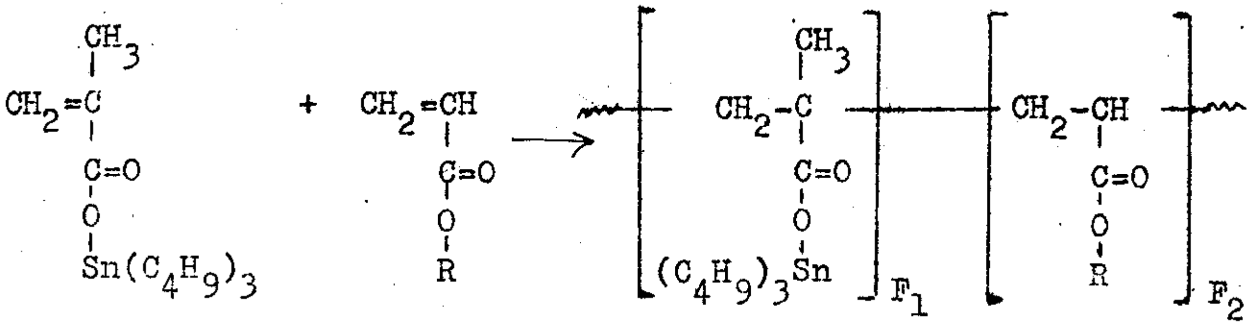


Fig. (9). I.R Spectrum for TBTMA – AMA copolymer.

CHAPTER V

Monomer reactivity ratios for copolymerizations of tri-n-butyltin methacrylate (TBTMA) with methyl acrylate (MA), ethyl acrylate (EA) and n-butyl acrylate (BA)

The copolymerization reactions of TBTMA with alkyl esters of acrylic acid can be represented as :



where R = $-CH_3$, $-C_2H_5$ or $n-C_4H_9$.

The experimental conditions and the results of the copolymerization reactions are illustrated in Tables 10-12.

Fig. (10) shows the Fineman-Ross plots of a-a/b as a function of a^2/b for the copolymerization of TBTMA with MA, EA and BA. The slope of the straight line of each system is equal to r_1 and the intercept gives $-r_2$.

Also, Fig. (11) illustrates the Kelen-Tüdős plots of the three systems which give r_1 and $-r_2/\alpha$ both as intercepts.

From the experimental data tabulated in tables 10-12 and figures 10, 11 for the copolymerization of TBTMA with MA, EA and BA, the monomer reactivity ratios calculated by both Fineman-Ross and Kelen-Tüdös methods are summarized in table (13). It is clear that there is a good agreement between the monomer reactivity ratios calculated by the two methods, and the experimental errors in r_1 and r_2 are quite small.

From the reactivity ratios of the three systems for the copolymerization of TBTMA with the alkyl esters of acrylic acid given in Table (13), it is clear that the copolymers should have random distribution of the monomer units in the copolymer molecules, and the tendency towards alternation increases with increasing the alkyl chain length of acrylic acid esters. Table (13) also shows that the monomer reactivity ratios determined for the copolymerization of TBTMA with BA is less than unity and should have azeotropic copolymerization behaviour while the copolymerization of TBTMA with MA and EA gave no azeotropic copolymers. The azeotropic composition of TBTMA-BA system was calculated from the monomer reactivity ratios and was found to be at 73.53:26.47 mole ratio. These data are in agreement with the composition curves (Fig. 12) which shows the relation between F_1 (mole fraction of TBTMA in copolymer) versus f_1 (mole fraction of TBTMA in comonomer feed). From Fig. 12c, it is clear that the curve crossed the line representing $F_1 = f_1$ at 0.74 mole fraction for copolymerization of TBTMA with BA.

Table (10)

Copolymerization of TBTMA (M_1) with MA (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.6997$	
$a^{(*)}$	$f_1^{(o)}$			$b^{(*)}$	$F_1^{(o)}$	$a - a/b$	a^2/b	η	ε
5.4861	0.8456	7.00	30.99	9.5151	0.9049	4.9096	3.1630	1.2709	0.8189
4.0141	0.8006	6.61	30.69	6.7358	0.8707	3.4182	2.3920	1.1055	0.7737
2.9435	0.7464	10.83	30.39	5.1456	0.8535	2.3715	1.6838	0.9949	0.7064
2.3383	0.7005	11.94	29.96	3.8865	0.7953	1.7367	1.4068	0.8244	0.6678
1.5006	0.6001	9.52	29.15	2.5893	0.7214	0.9211	0.8696	0.5869	0.5541
0.9981	0.4994	3.53	27.65	1.5537	0.6084	0.3557	0.6411	0.2653	0.4782
0.6605	0.3978	10.04	26.27	1.0984	0.5235	0.0592	0.3971	0.0539	0.3621
0.4316	0.3015	9.24	23.71	0.6782	0.4041	-0.2047	0.2747	-0.2102	0.2819
0.2531	0.2019	10.48	20.42	0.4139	0.2927	-0.3584	0.1548	-0.4194	0.1812

(*) Molar ratio (o) Mole fraction

Table (11)

Copolymerization of TBTMA (M_1) with EA (M_2)

Initial monomer composition		Coversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.6737$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ξ
5.4681	0.8454	10.03	30.59	7.0590	0.8759	4.6936	4.2350	0.9560	0.8628
3.7541	0.7896	7.64	30.10	4.9000	0.8305	2.9880	2.8760	0.8417	0.8102
2.9048	0.7442	9.31	29.73	3.9513	0.7980	2.1696	2.1354	0.7723	0.7602
2.2913	0.6917	9.80	29.21	3.0790	0.7548	1.5472	1.7049	0.6504	0.7168
1.5000	0.6000	8.10	28.17	2.1159	0.6793	0.7911	1.0630	0.5003	0.6122
0.9636	0.4908	7.03	26.58	1.3724	0.5785	0.2615	0.6765	0.1936	0.5011
0.6424	0.3912	10.40	24.24	0.8621	0.4633	-0.1027	0.4786	-0.0892	0.4154
0.4141	0.2928	9.09	21.90	0.5936	0.3725	-0.2835	0.2888	-0.2945	0.3001
0.1742	0.1483	9.20	16.35	0.2832	0.2207	-0.4409	0.1071	-0.5648	0.1370

(*) Molar ratio (°) Mole fraction

Table (12)

Copolymerization of TBTMA (M_1) with BA (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 1.0261$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	γ	ε
5.6498	0.8498	11.02	29.79	5.2374	0.8397	4.5710	6.0946	0.6419	0.8559
4.0098	0.8003	10.34	29.15	3.8574	0.7941	2.9701	4.1675	0.5718	0.8025
3.0156	0.7509	8.28	28.48	2.9730	0.7483	2.0013	3.0588	0.4899	0.7488
2.2950	0.6965	7.32	27.75	2.3758	0.7038	1.3290	2.2169	0.4098	0.6836
1;4986	0.5997	4.53	26.40	1.6878	0.6297	0.6107	1.3300	0.2591	0.5646
0.9943	0.4984	10.55	24.40	1.1358	0.5318	0.1188	0.8688	0.0627	0.4585
0.6649	0.3994	9.71	22.57	0.8408	0.4568	-0.1250	0.5257	-0.0811	0.3388
0.4301	0.3000	3.63	19.91	0.5749	0.3650	-0.3180	0.3217	-0.2359	0.2387
0.2528	0.2018	8.82	16.53	0.3699	0.2700	-0.4306	0.1727	-0.3592	0.1441

(*) Molar ratio (∘) Mole fraction

Table (13)

Monomer reactivity ratios in copolymerization of

TBTMA with MA, EA and BA

$M_1 - M_2$	Fineman-Ross method			Kelen-Tüdős method		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
TBTMA - MA	1.747 ± 0.028	0.644 ± 0.004	1.160	1.730 ± 0.025	0.649 ± 0.024	1.120
TBTMA - EA	1.259 ± 0.016	0.606 ± 0.032	0.763	1.262 ± 0.014	0.613 ± 0.024	0.773
TBTMA - BA	0.846 ± 0.005	0.572 ± 0.015	0.484	0.855 ± 0.008	0.578 ± 0.008	0.494

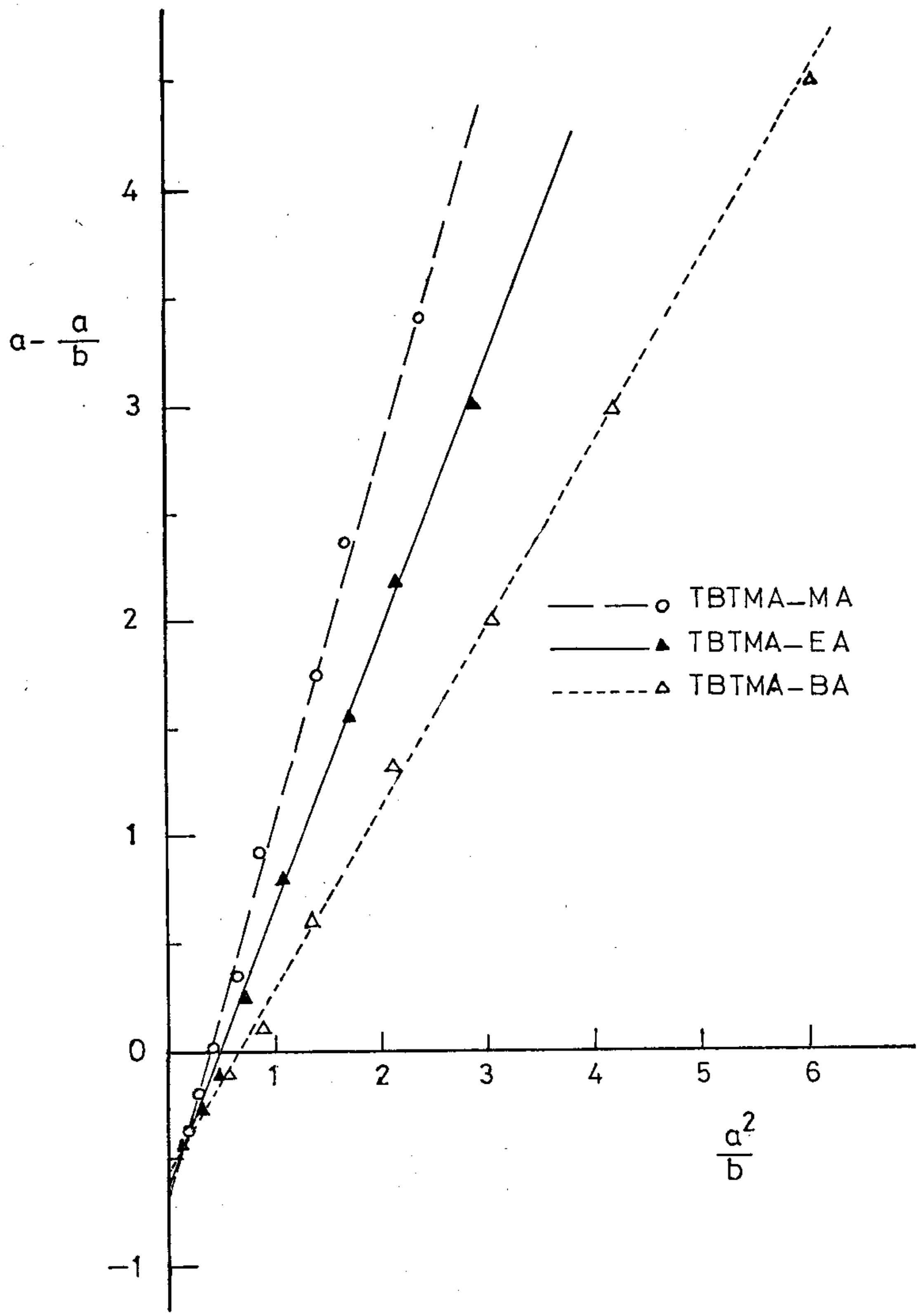


Fig. (10). Fineman–Ross plots for the copolymerization of: TBTMA–MA, TBTMA–EA, and TBTMA–BA.

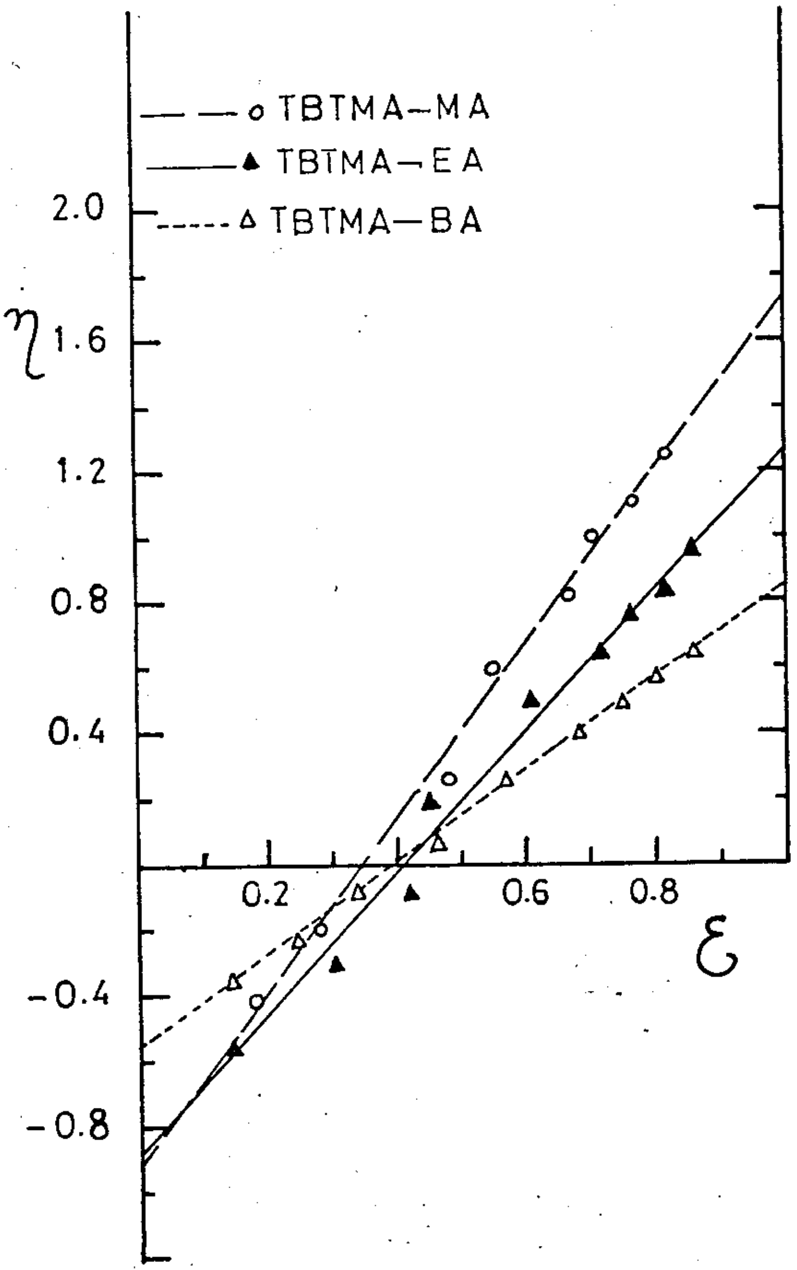


Fig. (11). kelen–Tüdős plots for the copolymerization of: TBTMA–MA, TBTMA–EA, and TBTMA–BA.

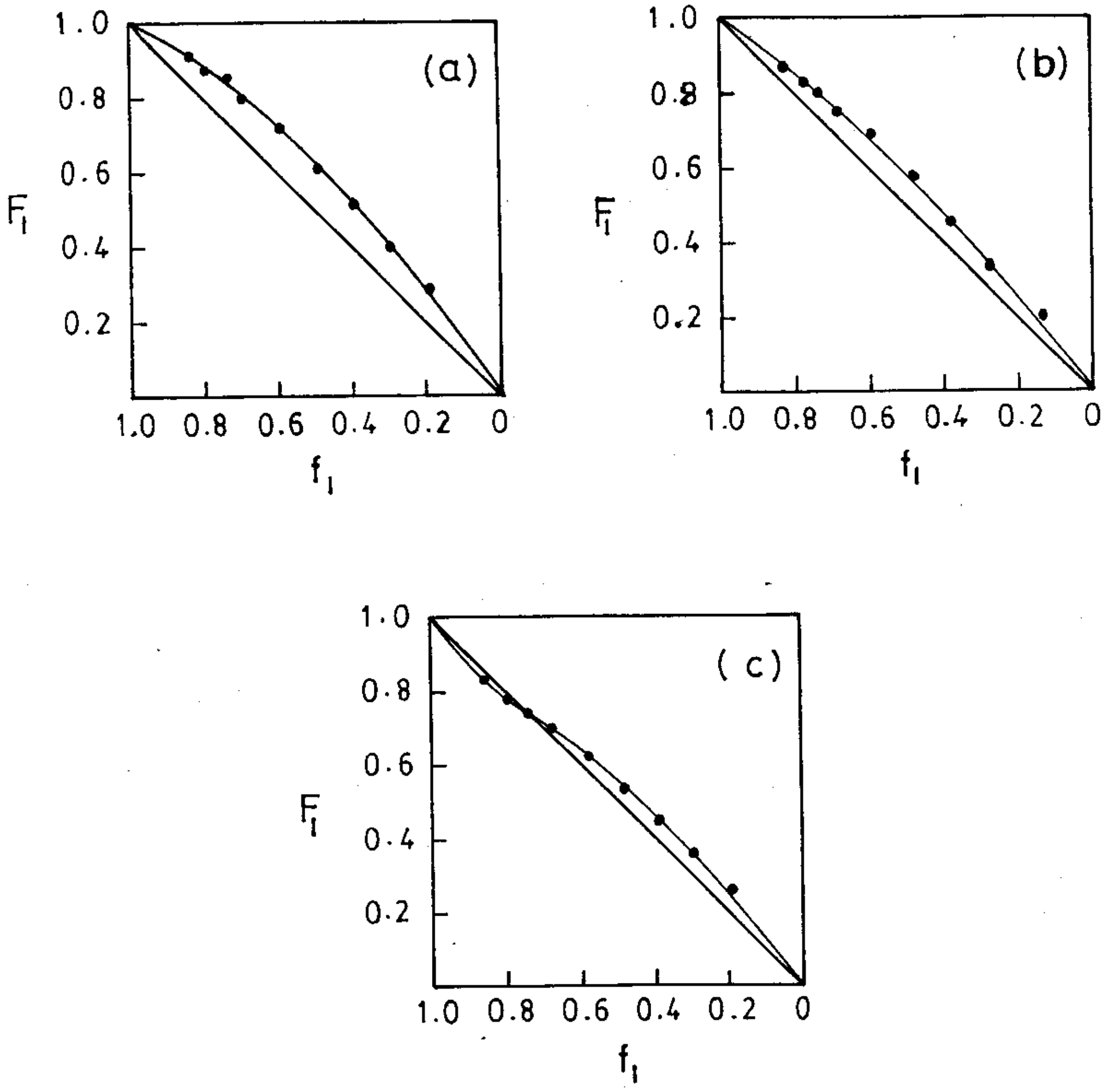


Fig. (12). Composition curves for the copolymerization of (a) TBTMA–MA, (b) TBTMA–EA, and (c) TBTMA–BA. f_1 = mole fraction of M_1 in feed and F_1 = mole fraction of M_1 in copolymer.

This point of intersection corresponds to the azeotropic composition yielding homogeneous copolymer regardless of conversion.

The azeotropic comonomer composition of TBTMA-BA system was polymerized; by solution copolymerization in toluene in presence of 1 mole % AIBN at 70°C to several conversions covering a wide range. Table (14) illustrates the experimental conditions and the results for azeotropic copolymerization of TBTMA with BA. (Fig. (13) shows the relation between percent conversion versus time for the azeotropic mixture of TBTMA and BA. Fig. (14) shows F_1 (mole fraction of TBTMA in copolmyer) against % conversion and indicates that the experimental points, calculated from the tin content of each sample, are in good agreement with the line representing the azeotropic composition. From Table (14), and Fig. (14), it is clear that the azeotropic copolymer composition of TBTMA-BA remains constant up to 90 % conversion, and the tin content of the copolymer gave a mean value of 28.28 % against a calculated value of 28.26 % for the azeotropic composition.

The sequence distribution of the monomers at the azeotropic composition of the TBTMA-BA system was calculated from the normograph of Izu and O'Driscol[61]. Thus, the triad fractions for the azeotropic copolymer of TBTMA-BA was found to be as follows:

f_{111}	f_{112}	f_{121}	f_{212}
0.3818	0.1522	0.1794	0.0606

Table (14)

Azeotropic copolymerization of TBTMA (M_1) with BA (M_2)

		Mole fraction	gram
TBTMA	=	0.7353	27.5738
BA	=	0.2647	3.3882
AIBN	=	(1 mole %)	0.1640

Solution polymerization in toluene (3 Moles/L, total volume 33.33 ml).

Time (minutes)	Conversion %	Sn %	F_1
5	15.02	28.17	0.7398
10	37.04	28.02	0.7205
20	65.83	28.39	0.7437
40	77.98	28.49	0.7501
60	89.96	28.31	0.7386

The structure of the prepared copolymers of tri-n-butyltin methacrylate with the alkyl esters of acrylic acid was investigated by infrared spectroscopy and was found to be quite similar in the region between 400 cm^{-1} to 1400 cm^{-1}. Also, the IR spectra of these copolymers are characterized by the presence of two strong bands at 1645 cm^{-1} and at 1738 cm^{-1} due to the stretching frequencies of the $\rangle C{=}O$ groups of the tri-n-butyltin carboxylates and the acrylic esters, respectively. The bands at 2860-2970 cm^{-1} are due to the symmetrical and assymetrical stretching frequencies of the C-H bonds due to $-CH_2$ and $-CH_3$ groups. Fig. (15) illustrates the IR spectrum of TBTMA-BA azeotropic copolymer as an example of the studied copolymerizations of TBTMA with alkyl acrylates.

Copolymers prepared from the reaction of TBTMA with alkyl acrylates are clear, transparent and soluble in most organic solvents even at high conversions except the alcohols methanol and ethanol. Films prepared from the copolymers of TBTMA-MA, TBTMA-EA and TBTMA-BA exerted some tackiness which might limit their use as binders for antifouling coatings. To improve the film properties, the copolymers were prepared at various lower initiator concentrations ranging from 0.25 to 0.05 mole/100 moles monomers, but the tackiness of the films was only a little improved. The viscosity measurements of the azeotropic copolymer are illustrated in Table (15) which shows that the reduced viscosity of the azeotropic copolymer (TBTMA-BA), 1 % solution in toluene at 30°C, increases with decreasing the initiator concentration. The tackiness of the copolymer and the relatively low reduced viscosity values may be due to a chain transfer effect with the solvent (toluene).[62]

Table (15)

Initiator concentration	$\eta_{sp/c}$
1 mole %	0.1989
0.25 mole %	0.2159
0.10 "	0.2381
0.05 "	0.3115

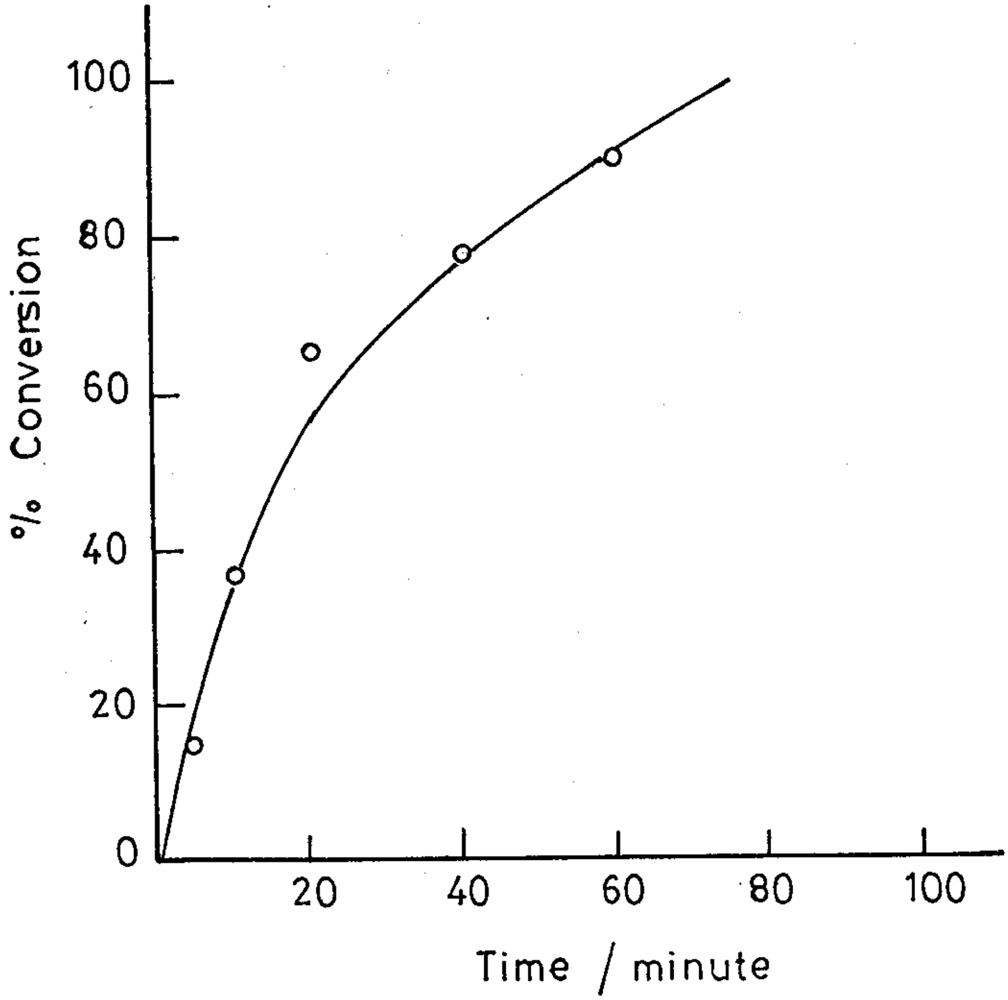


Fig. (13). Variation in percent azeotropic copolymer produced with time for azeotropic copolymerization of TBTMA — BA.

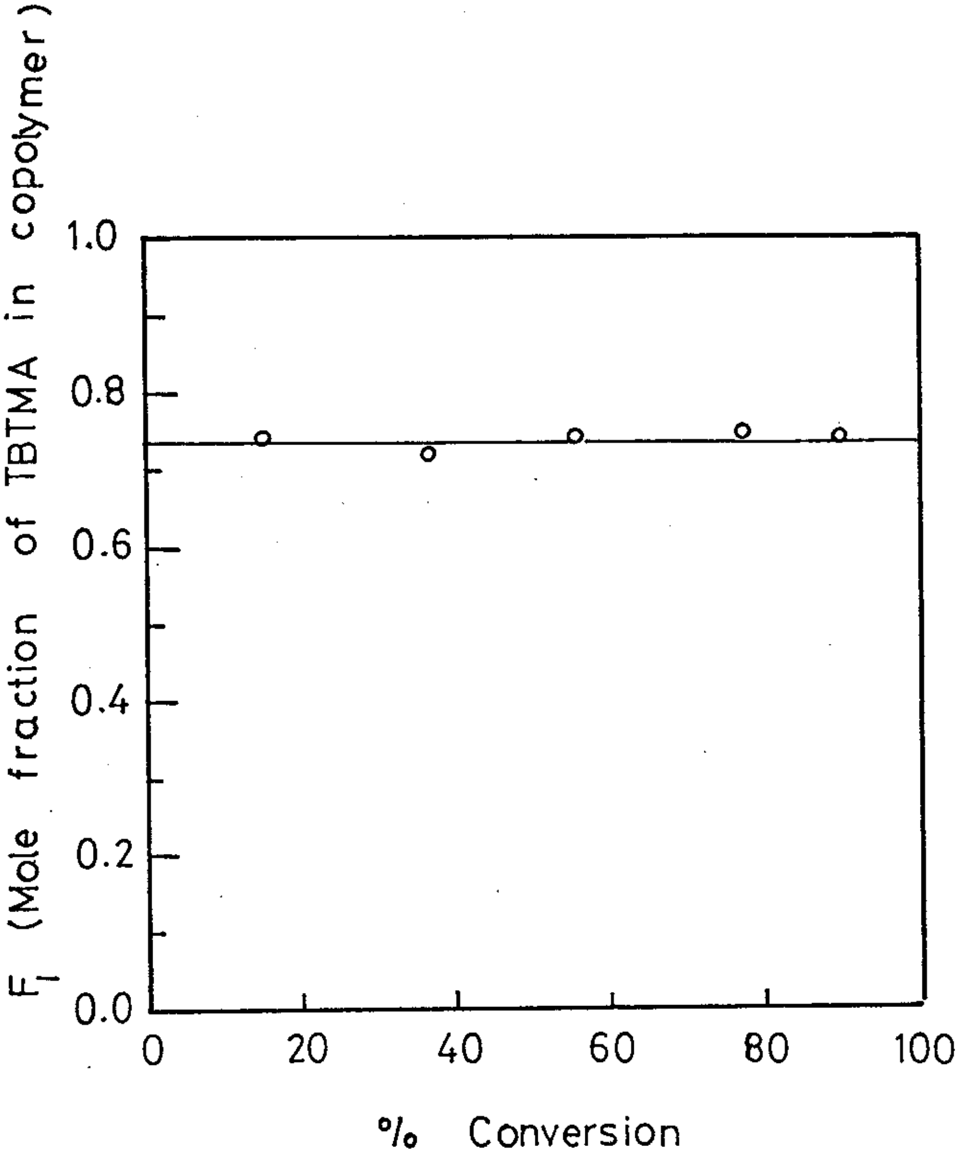


Fig. (14). F_1 as a function of conversion for azeotropic copolymerization of TBTMA– BA

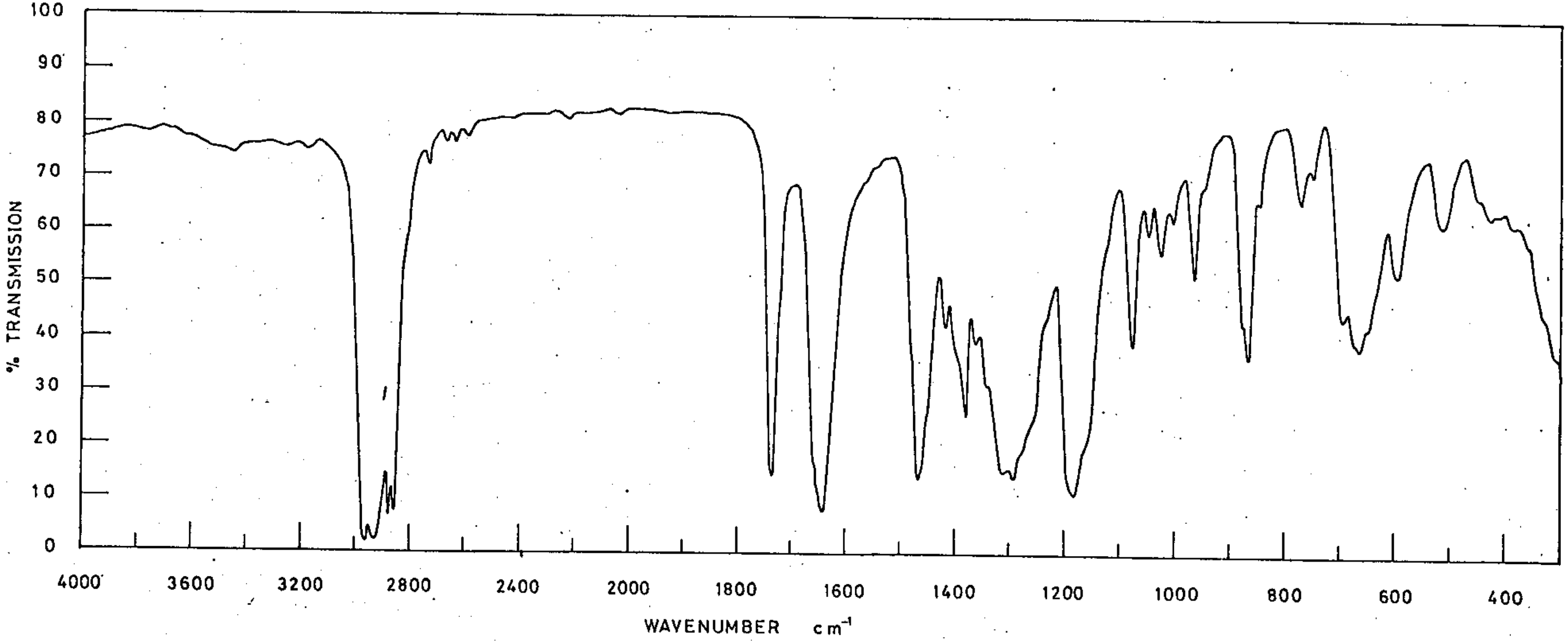
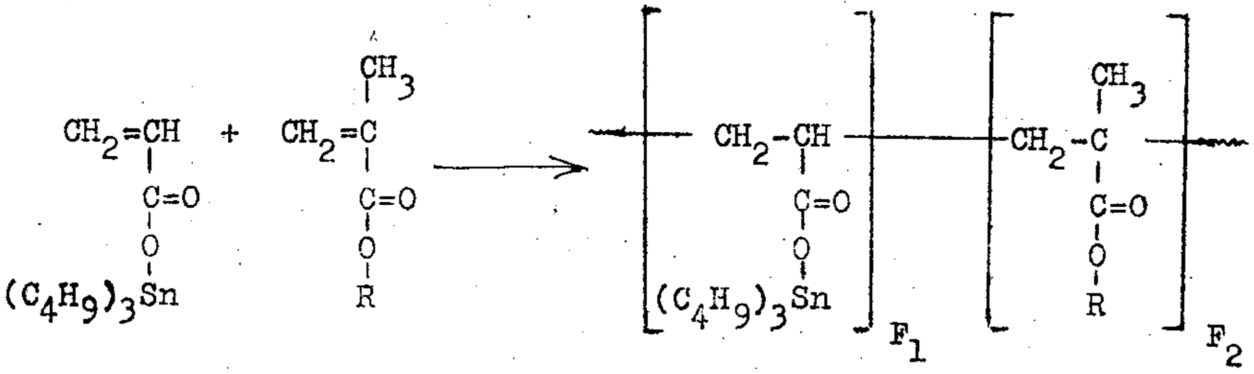


Fig. (15). I.R Spectrum for TBTMA–BA copolymer.

CHAPTER VI

Monomer reactivity ratios for copolymerizations of tri-n-butyltin acrylate (TBTA) with methyl methacrylate (MMA), n-propyl methacrylate (PrMA), n-butyl methacrylate (BMA) and allyl methacrylate (AMA)

The copolymerization reactions of TBTA with the alkyl esters of methacrylic acid and allyl methacrylate can be represented as :



$$CH_2{=}CH(C{=}O)O\,Sn(C_4H_9)_3 + CH_2{=}C(CH_3)(C{=}O)OR \longrightarrow -\left[CH_2-CH(C{=}O)O\,Sn(C_4H_9)_3\right]_{F_1}-\left[CH_2-C(CH_3)(C{=}O)OR\right]_{F_2}-$$

where R = $-CH_3$, $n-C_3H_7$, $n-C_5H_9$ and $-CH_2-CH{=}CH_2$.

The experimental conditions and the results of the copolymerization reactions are illustrated in Tables (16-19).

Fig. (16) shows the Fineman-Ross plots of a-a/b as a function of a^2/b for the copolymerizations of TBTA with MMA, PrMA, BMA and AMA. The slope of the straight line of each system is equal to r_1 and the intercept gives $-r_2$. Also, Fig. (17) illustrates the Kelen-Tüdos plots of the four systems which give r_1 and $-r_2/\alpha$ both as intercepts.

From the experimental data tabulated in Tables (16-19) and Figs. 16 and 17) for the copolymerization of TBTA with MMA, PrMA, BMA and AMA, the monomer reactivity ratios calculated by both Fineman-Ross and Kelen-Tüdos methods are summarized in Table (20). The data illustrated in Table (20) show that there is a good agreement between the monomer reactivity ratios calculated by the two methods, and the experimental errors in r_1 and r_2 are in a small range within the experimental error.

From the reactivity ratios of the four systems for the copolymerization of TBTA with the alkyl esters of methacrylic acid and allyl methacrylate tabulated in Table (20), it is clear that the copolymers should have random distribution of the monomer units in the copolymer molecules, and the tendency towards alternation increases with increasing the alkyl chain length of methacrylic acid esters. This behaviour is in agreement with the data obtained on copolymerization of TBTMA with alkyl methacrylates and alkyl acrylates, and with the work of Zabotin and Malysheva[45] on emulsion copolymerization of TBTA with alkyl acrylates using $K_2S_2O_8$ as initiator. Table (20) also shows that the copolymerization of TBTA with MMA, PrMA, BMA and AMA gave no azeotropic copolymers (r_2 values are always greater than unity). Also, the composition curves illustrated in Fig. (18) show that the four systems gave no azeotropic copolymers.

Table (16)

Copolymerization of TBTA (M_1) with MMA (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 3.4621$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ξ
8.3634	0.8932	11.91	30.22	3.0553	0.7534	5.6261	22.8935	0.2135	0.8686
4.2636	0.8100	8.52	28.51	1.7746	0.6396	1.8610	10.2436	0.1358	0.7474
2.8922	0.7431	6.23	26.96	1.2447	0.5545	0.5686	6.7203	0.0558	0.6599
2.2893	0.6959	5.64	25.76	0.9911	0.4978	-0.0206	5.2879	-0.0023	0.6043
1;5169	0.6027	9.43	23.23	0.6613	0.3981	-0.7769	3.4795	-0.1119	0.5013
0.9854	0.4963	7.64	19.64	0.4085	0.2900	-1.4268	2.3769	-0.2444	0.4071
0.6727	0.4022	8.13	16.92	0.2922	0.2261	-1.6295	1.5486	-0.3252	0.3091
0.4251	0.2983	7.98	13.34	0.1883	0.1585	-1.8395	0.9596	-0.4144	0.2170
0.2494	0.1996	8.26	9.89	0.1188	0.1062	-1.8499	0.5236	-0.4641	0.1398

(*) Molar ratio (○) Mole fraction

Table (17)

Copolymerization of TBTA (M_1) with PrMA (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 3.2234$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ξ
5.9176	0.8554	9.85	28.06	2.0305	0.6700	3.0032	17.2464	0.1467	0.8425
4.0439	0.8017	9.13	27.14	1.6534	0.6231	1.5981	9.8906	0.1219	0.7542
2.9799	0.7487	8.25	25.51	1.2141	0.5484	0.5255	7.3139	0.0499	0.6941
2.2936	0.6964	10.32	24.26	0.9887	0.4972	-0.0262	5.3207	-0.0031	0.6227
1.5172	0.6027	7.92	21.80	0.6917	0.4089	-0.6762	3.3279	-0.1032	0.5080
0.9952	0.4988	8.87	19.08	0.4874	0.3277	-1.0466	2.0320	-0.1992	0.3867
0.6631	0.3987	9.79	15.88	0.3297	0.2479	-1.3480	1.3333	-0.2958	0.2926
0.4291	0.3003	8.63	13.21	0.2372	0.1917	-1.3799	0.7761	-0.3450	0.1941
0.3334	0.2500	10.03	11.29	0.1845	0.1557	-1.4736	0.6024	-0.3852	0.1575

(*) Molar ratio (°) Mole fraction

Table (18)

Copolymerization of TBTA (M_1) with BMA (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 2.9145$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ξ
4.2388	0.8091	6.02	25.31	1.3014	0.5655	0.9817	13.8062	0.0587	0.8257
2.9759	0.7485	5.41	23.86	1.0314	0.5077	0.0906	8.5864	0.0079	0.7466
2.2279	0.6902	5.57	22.45	0.8402	0.4566	-0.4237	5.9075	-0.0480	0.6696
1.4664	0.5945	5.94	19.81	0.5926	0.3721	-1.0081	3.6286	-0.1541	0.5546
0.9937	0.4984	6.35	17.43	0.4415	0.3063	-1.2570	2.2365	-0.2440	0.4342
0.6370	0.3891	5.48	14.67	0.3155	0.2398	-1.3820	1.2862	-0.3290	0.3062
0.5353	0.3487	6.55	13.06	0.2582	0.2052	-1.5379	1.1096	-0.3822	0.2757
0.4245	0.2980	3.89	12.04	0.2264	0.1846	-1.4505	0.7959	-0.3909	0.2145
0.3300	0.2481	4.97	10.23	0.1770	0.1504	-1.5344	0.6153	-0.4347	0.1743

(*) Molar ratio (○) Mole fraction

Table (19)

Copolymerization of TBTA (M_1) with AMA (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 5.1901$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ξ
5.5767	0.8479	8.23	26.43	1.4127	0.5855	1.6292	22.0143	0.0600	0.8088
3.9315	0.7972	7.57	24.83	1.0659	0.5159	0.2433	14.4999	0.0124	0.7364
2.8842	0.7425	9.64	23.38	0.8518	0.4599	-0.5018	9.7659	-0.0336	0.6529
2.3649	0.7028	9.28	22.08	0.7103	0.4153	-0.9645	7.8739	-0.0738	0.6027
1.4782	0.5965	8.18	18.81	0.4639	0.3169	-1.7078	4.7096	-0.1725	0.4757
0.9948	0.4987	8.37	16.13	0.3345	0.2507	-1.9792	2.9584	-0.2429	0.3631
0.6478	0.3931	9.05	12.91	0.2247	0.1835	-2.2351	1.8674	-0.3167	0.2646
0.4267	0.2991	8.53	9.85	0.1488	0.1295	-2.4409	1.2238	-0.3806	0.1908

(*) Molar ratio (∘) Mole fraction

Table (20)

Monomer reactivity ratios in copolymerization of TBTA with MMA, PrMA, BMA and AMA

M_1-M_2	Fineman-Ross method			Kelen-Tüdős method		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
TBTA-MMA	0.401±0.012	2.199+0.060	0.882	0.395±0.013	2.180±0.058	0.861
TBTA-PrMA	0.323±0.010	1.713±0.048	0.553	0.314±0.008	1.684±0.033	0.529
TBTA-BMA	0.196±0.005	1.661±0.032	0.326	0.197±0.005	1.668±0.028	0.329
TBTA-AMA	0.195±0.005	2.575±0.054	0.502	0.201±0.004	2.619±0.041	0.526

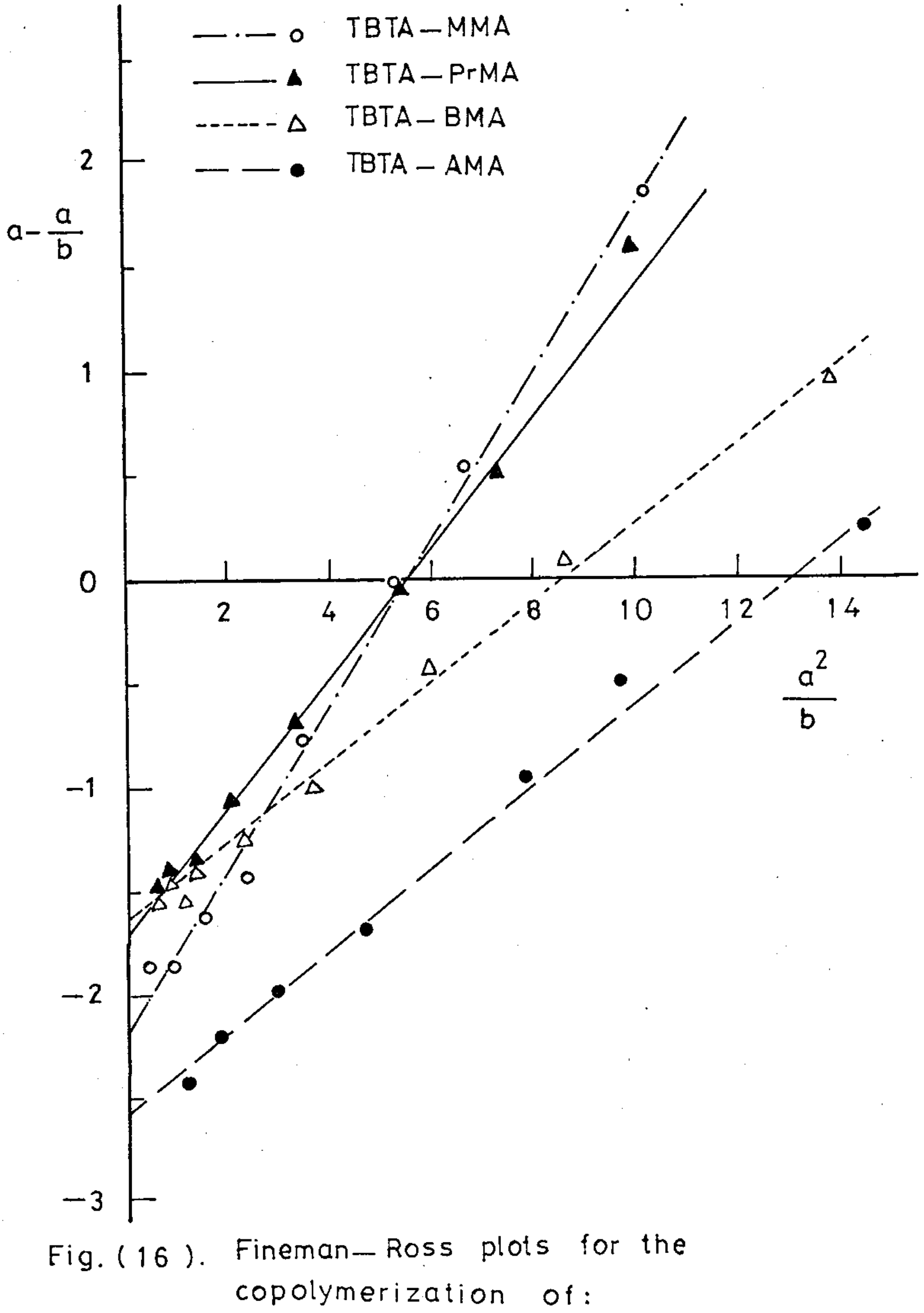


Fig. (16). Fineman— Ross plots for the copolymerization of: TBTA–MMA , TBTA – PrMA , TBTA–BMA , and TBTA–AMA.

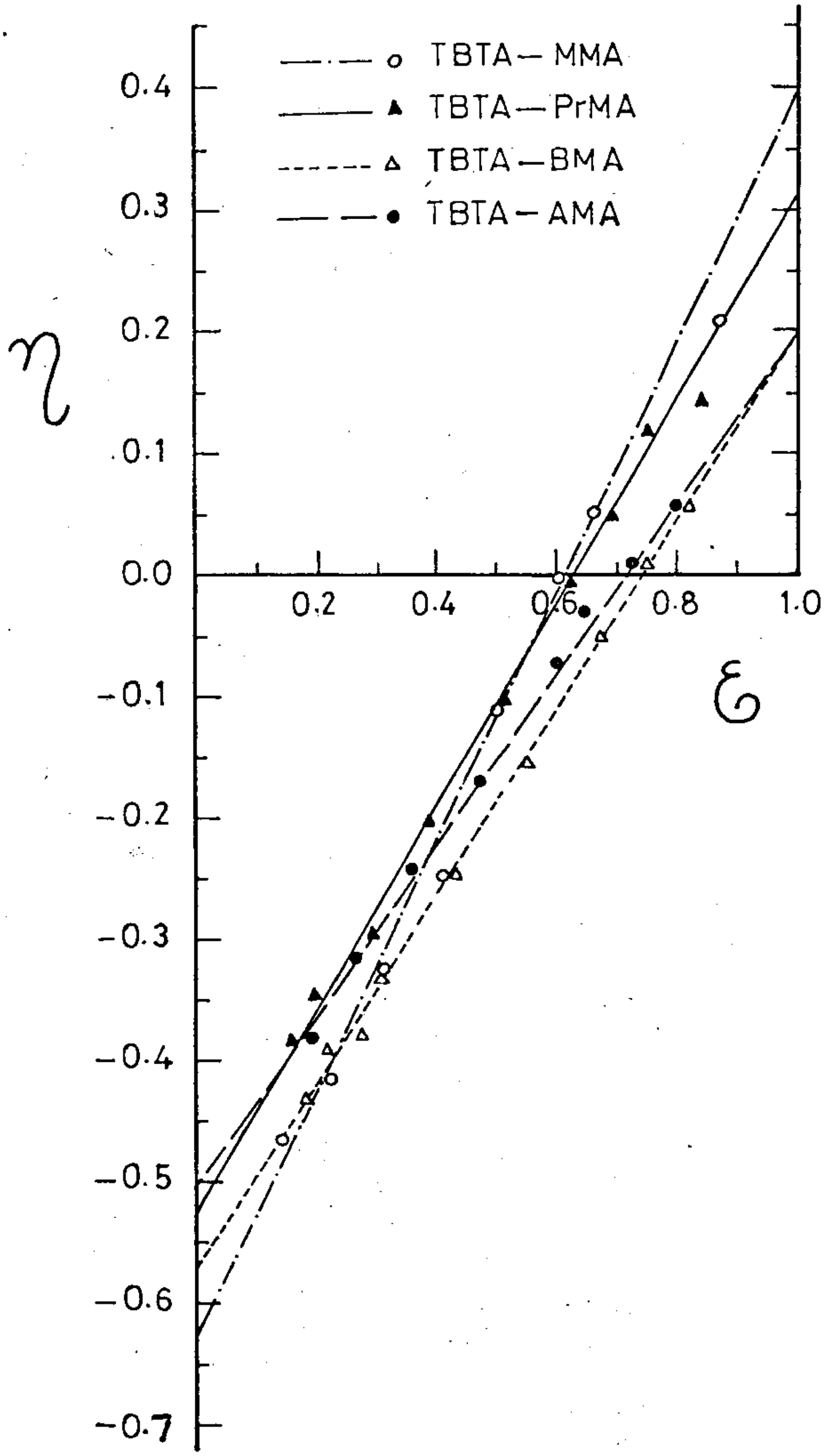


Fig. (17). Kelen–Tüdös plots for the copolymerization of: TBTA–MMA , TBTA–PrMA , TBTA–BMA , and TBTA–AMA.

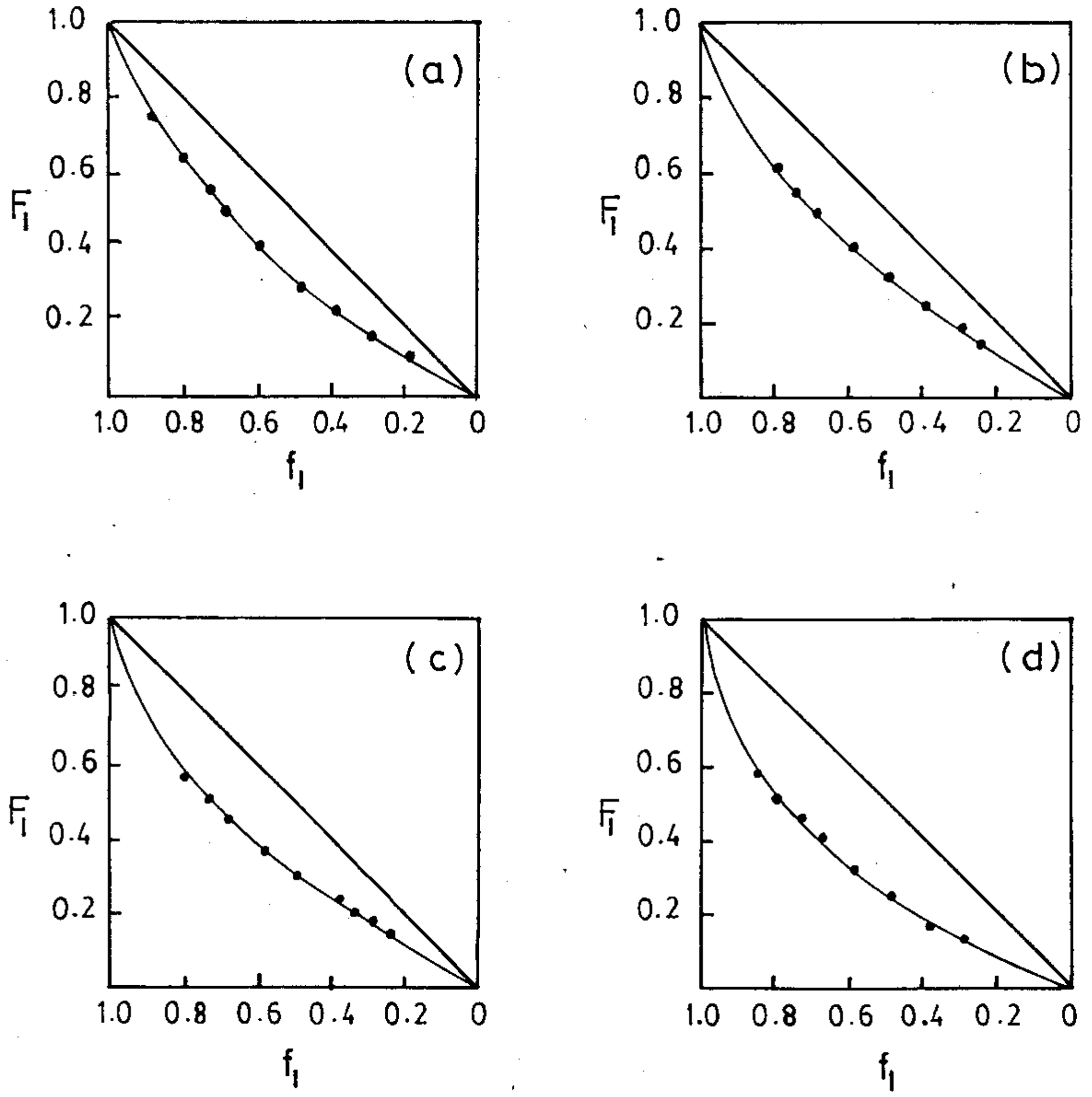


Fig. (18). Composition curves for the copolymerization of: (a) TBTA-MMA, (b) TBTA-PrMA, (c) TBTA-BMA, and (d) TBTA-AMA.

f_1 = mole fraction of M_1 in feed and

F_1 = mole fraction of M_1 in copolymer.

The correctness of the determined reactivity ratios was checked by studying the variation of copolymer composition with conversion. Thus, a feed composition of 30:70 mole % for TBTA-MMA and TBTA-BMA systems was polymerized over a wide range of conversion. Each sample at each level of conversion was analyzed for its tin content, from which the copolymer composition was calculated. Tables (21) and (22) illustrate the experimental conditions and results of both systems and Fig. (19) shows the conversion as a function of time for both systems. From the feed composition (30:70) and the determined reactivity ratios of these systems (Table 20), the variation of average copolymer composition with conversion was calculated by integration of the copolymer composition equation (page 17) according to the method described by Skeist[12], assuming that the copolymer composition within 10 % interval is constant. Fig. (20) shows good agreement between the calculated curves and the experimental points over a wide range of conversion indicating the correctness of the determined reactivity ratios of both systems.

The structure of the prepared copolymers of tri-n-butyltin acrylate with the alkyl esters of methacrylic acid as well as allyl methacrylate was investigated by infrared spectroscopy and the diagrams were found to be quite similar in the region

Table (21)

Variation of average copolymer composition for copolymerization of TBTA with BMA.

	Mole percent	gram
TBTA :	30	10.8300
BMA :	70	9.9400
AIBN :	(1 mole %)	0.1640

Solution polymerization in toluene (3 mole/1, total volume 33.33 ml).

Time (hour)	Conversion %	Sn %	Copolymer composition mole %	
			TBTA	BMA
0.5	22.20	12.30	18.96	81.04
1.0	43.22	12.80	19.97	80.03
2.0	65.96	13.81	22.09	77.91
3.0	74.92	13.97	22.40	77.60
4.0	85.32	14.24	23.01	76.99
5.0	92.40	15.11	24.90	75.10

Table (22)

Variation of average copolymer composition for copolymerization of TBTA with MMA

	Mole percent	gram
TBTA :	30	10.8300
MMA :	70	7.0000
AIBN :	(1 mole %)	0.1640

Solution polymerization in toluene (3 mole/l, total volume 33.33 ml).

Time (hour)	Conversion %	Sn %	Copolymer composition mole %	
			TBTA	MMA
0.5	18.90	13.90	16.79	83.21
1.0	36.70	14.56	17.96	82.04
2.0	62.50	15.24	19.23	80.77
3.0	75.40	16.38	21.47	78.53
4.0	81.90	17.20	23.20	76.80
5.0	95.5	17.70	24.30	75.70

between 400 cm^{-1} to 1400 cm^{-1}. Fig. (21) illustrates the IR spectrum of TBTA-PrMA copolymer as an example of this group and shows that these copolymers are characterized by the presence of two strong bands at 1650 cm^{-1} and at 1730 cm^{-1} due to the stretching frequencies of the $\rangle C=O$ groups of the tributyltin carboxylates and the methacrylic esters, respectively. The bands at 2880-2970 cm^{-1} are due to the symmetrical and assymmetrical stretching frequencies of the C-H bonds due to the CH_2 and $-CH_3$ groups.

Copolymers prepared from the reaction of TBTA with alkyl methacrylates are clear, transparent, and soluble in most organic solvents even at higher conversions, while the copolymer of TBTA with AMA gave an insoluble gel product at higher conversions. Also, copolymers produced from TBTA with MMA were clear solids suitable for film formation while those from TBTA with both PrMA and BMA were rubbery and tacky products.

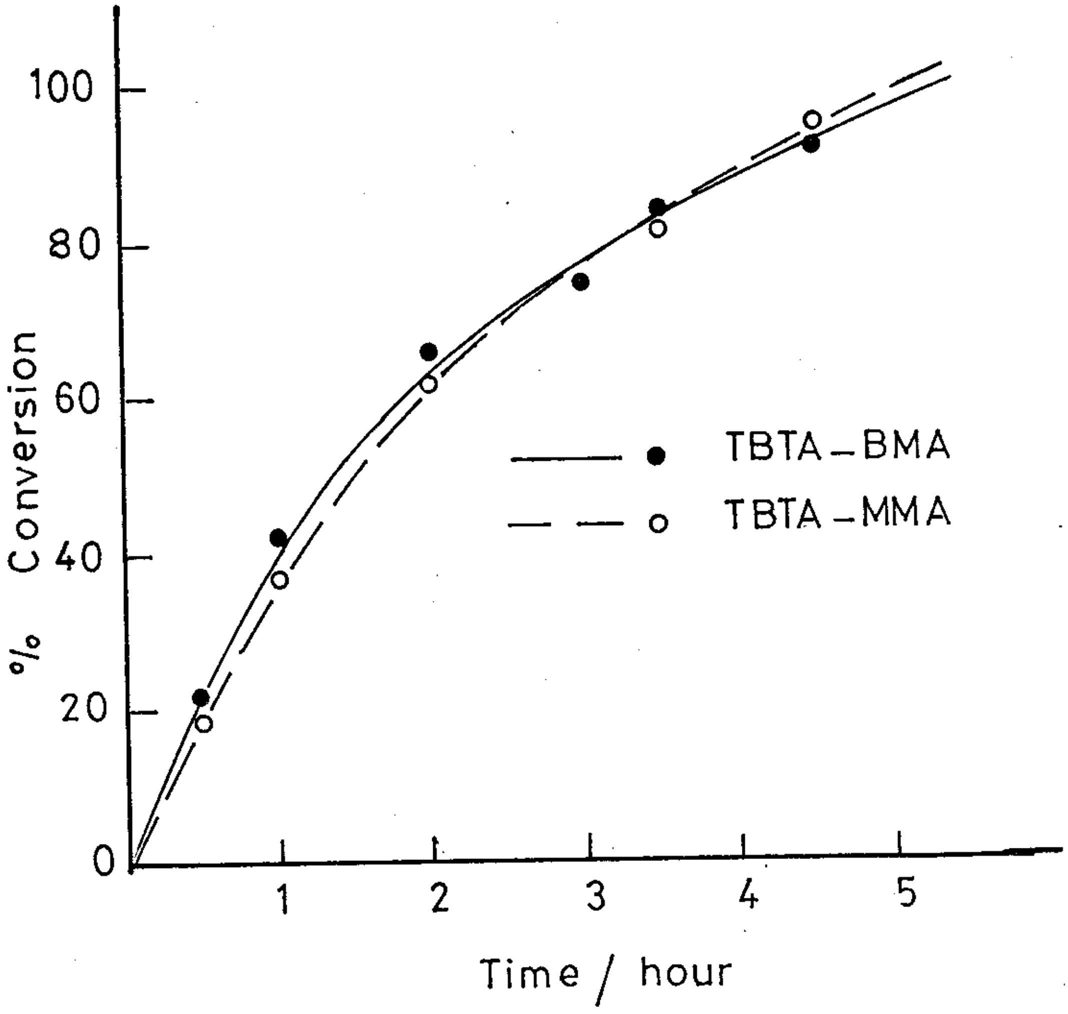


Fig. (19). Variation in percent copolymers produced with time for : TBTA – MMA and TBTA – BMA .

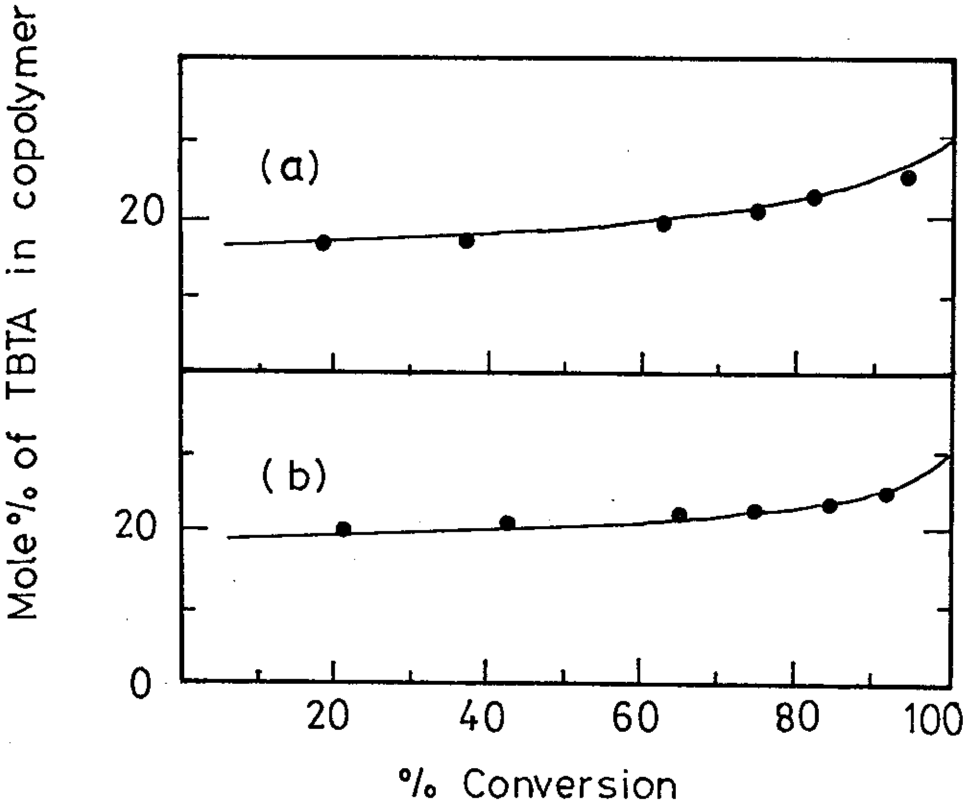


Fig. (20). Average copolymer composition with conversion for: (a) TBTA–MMA and (b) TBTA–BMA, lines represent calculated copolymer composition and (●) from tin analysis.

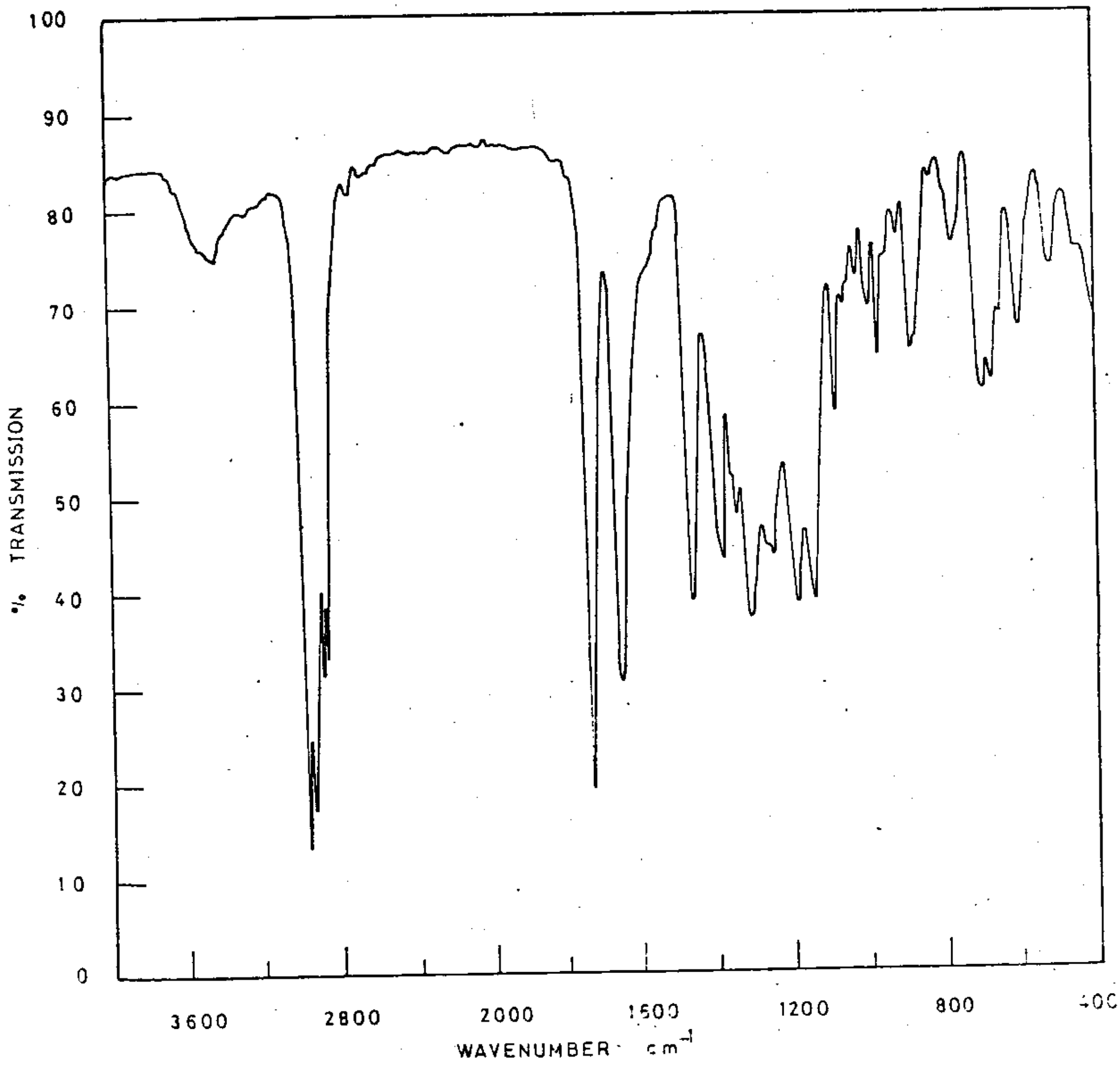
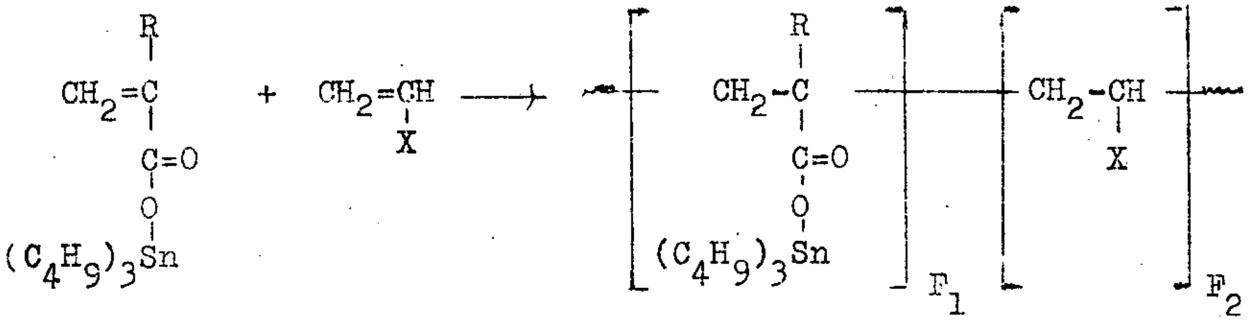


Fig. (21). I.R Spectrum for TBTA—PrMA copolymer.

CHAPTER VII

Monomer reactivity ratios for copolymerizations of tri-n-butyltin acrylate and methacrylate with acrylonitrile (AN) and styrene (St).

The copolymerization reactions of both TBTMA and TBTA with St and AN can be represented as :



where R = H or $-CH_3$, and X = $-C_6H_5$ or $-C{\equiv}N$.

The experimental conditions and the results of the copolymerization reactions are illustrated in Tables (23-26).

Fig. (22) shows the Fineman-Ross plots for the copolymerizations of TBTMA and TBTA with AN and St. Also Fig. (23) illustrates the Kelen-Tüdos plots of the four systems.

From the experimental data tabulated in Tables (23-26) and figures (22 & 23) for the copolymerization of TBTMA and TBTA with AN and St, the monomer reactivity ratios calculated by both Fineman-Ross and Kelen-Tüdos methods are summarized in Table (27).

Table (23)

Copolymerization of TBTMA (M_1) with AN (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 0.7046$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ξ
2.3150	0.6330	8.23	29.34	1.7258	0.6982	0.9735	3.1060	0.2555	0.8151
1.8474	0.5953	7.94	28.96	1.4721	0.6487	0.5925	2.3184	0.1959	0.7669
1.4854	0.5642	9.95	28.61	1.2946	0.5976	0.3381	1.7042	0.1403	0.7075
1.2245	0.5353	8.74	28.27	1.1519	0.5504	0.1615	1.3018	0.0805	0.6488
1.0034	0.5055	6.27	27.88	1.0225	0.5009	0.0221	0.9847	0.0131	0.5829
0.8272	0.4669	5.69	27.33	0.8761	0.4527	-0.1169	0.7809	-0.0787	0.5257
0.6617	0.4314	8.78	26.75	0.7586	0.3981	-0.2106	0.5771	-0.1643	0.4503
0.5455	0.4018	7.89	26.22	0.6720	0.3530	-0.2662	0.4428	-0.2320	0.3859
0.4329	0.3624	9.35	25.42	0.5685	0.3021	-0.3286	0.3296	-0.3177	0.3188
0.2491	0.2795	7.48	23.27	0.3881	0.1994	-0.3927	0.1599	-0.4542	0.1851

(*) Molar ratio (∘) Mole fraction

Table (24)

Copolymerization of TBTMA (M_1) with St (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 1.1491$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	a-a/b	a^2/b	η	ξ
4.000	0.8000	8.12	26.98	1.5910	0.6140	1.4859	10.0566	0.1326	0.8975
2.3300	0.6999	10.16	25.21	1.0726	0.5175	0.1577	5.0614	0.0254	0.8150
1.5000	0.60000	6.00	23.56	0.7970	0.4435	-0.3799	2.8199	-0.0957	0.7105
1.0000	0.5000	8.92	21.83	0.6134	0.3802	-0.6303	1.6303	-0.2268	0.5866
0.6667	0.4000	8.24	19.39	0.4354	0.3033	-0.8645	1.0209	-0.3984	0.4705
0.4286	0.3000	8.83	16.79	0.3120	0.2378	-0.9451	0.5888	-0.5438	0.3388
0.2500	0.2000	9.81	13.07	0.1946	0.1628	-1.0347	0.3212	-0.7033	0.2185
0.1111	0.0999	9.62	8.00	0.0937	0.0856	-1.0746	0.1313	-0.8393	0.1025

(*) Molar ratio (∘) Mole fraction

Table (25)

Copolymerization of TBTA (M_1) with AN (M_2)

Initial monomer composition		Conversion	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 2.8824$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ε
9.0000	0.9000	6.35	31.36	2.8672	0.7414	5.8611	28.2500	0.1883	0.9074
3.9973	0.7998	7.53	30.14	1.5691	0.6108	1.4498	10.1830	0.1109	0.7794
2.9255	0.7453	9/31	29.54	1.2723	0.5599	0.6263	6.7314	0.0652	0.7002
2.3220	0.6989	8.07	28.98	1.0691	0.5166	0.1501	5.0432	0.0189	0.6363
1.3728	0.6519	8.49	28.56	0.9529	0.4879	-0.0926	3.6809	-0.0141	0.5608
1.5062	0.6009	9.14	27.94	0.8171	0.4497	-0.3371	2.7765	-0.0596	0.4906
P/9858	0.4964	9.93	26.63	0.6165	0.3814	-0.6132	1.5762	-0.1375	0.3535
0.6638	0.3989	8.45	25.03	0.4634	0.3166	-0.7689	0.9508	-0.2005	0.2480
0.4244	0.2979	10.01	22.84	0.3344	0.2489	-0.8563	0.5434	-0.2499	0.1586
0.2492	0.1995	8.27	19.45	0.2112	0.1745	-0.9297	0.2937	-0.2931	0.0926

(*) Molar ratio (∘) Mole fraction

Table (26)

Copolymerization of TBTA (M_1) with St (M_2)

Initial monomer composition		Conversion %	Sn %	Copolymer composition		Fineman-Ross method		Kelen-Tüdős method $\alpha = 1.1559$	
$a^{(*)}$	$f_1^{(\circ)}$			$b^{(*)}$	$F_1^{(\circ)}$	$a-a/b$	a^2/b	η	ξ
4.0000	0.8000	10.24	26.79	1.2562	0.5567	0.8158	12.7568	0.0587	0.9168
2.3300	0.6997	10.42	24.48	0.8298	0.4534	0.4779	6.5424	-0.0621	0.8499
1.5000	0.6000	7.51	21.93	0.5741	0.3647	-1.1128	3.9192	-0.2193	0.7722
1.0000	0.5000	6.62	19.48	0.4166	0.2940	-1.4004	2.4004	-0.3938	0.6749
0.6667	0.4000	10.25	16.66	0.2946	0.2275	-1.5960	1.5088	-0.5989	0.5662
0.4286	0.3000	10.01	13.56	0.2009	0.1666	-1.7048	0.9144	-0.8235	0.4417
0.2500	0.2000	10.02	9.89	0.1240	0.1103	-1.7661	0.5040	-1.1304	0.3036
0.1111	0.1000	11.34	5.39	0.0559	0.0529	-1.8763	0.2200	-1.3637	0.1599
0.0526	0.0500	9.51	2.79	0.0267	0.0260	-1.9174	0.1049	-1.5208	0.0832

(*) Molar ratio (∘) Mole fraction

Table (27)

Monomer reactivity ratios in copolymerization of
TBTMA and TBTA with AN and St.

M_1-M_2	Fineman-Ross method			Kelen-Tüdős method		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
TBTMA-AN	0.465±0.006	0.467±0.009	0.217	0.471±0.007	0.474±0.008	0.223
TBTMA-St	0.256±0.003	1.104±0.039	0.283	0.259±0.004	1.108±0.009	0.287
TBTA-AN	0.243±0.001	1.008±0.011	0.245	0.240±0.001	0.997±0.007	0.239
TBTA-St	0.213±0.010	1.910±0.049	0.407	0.219±0.013	1.939±0.038	0.425

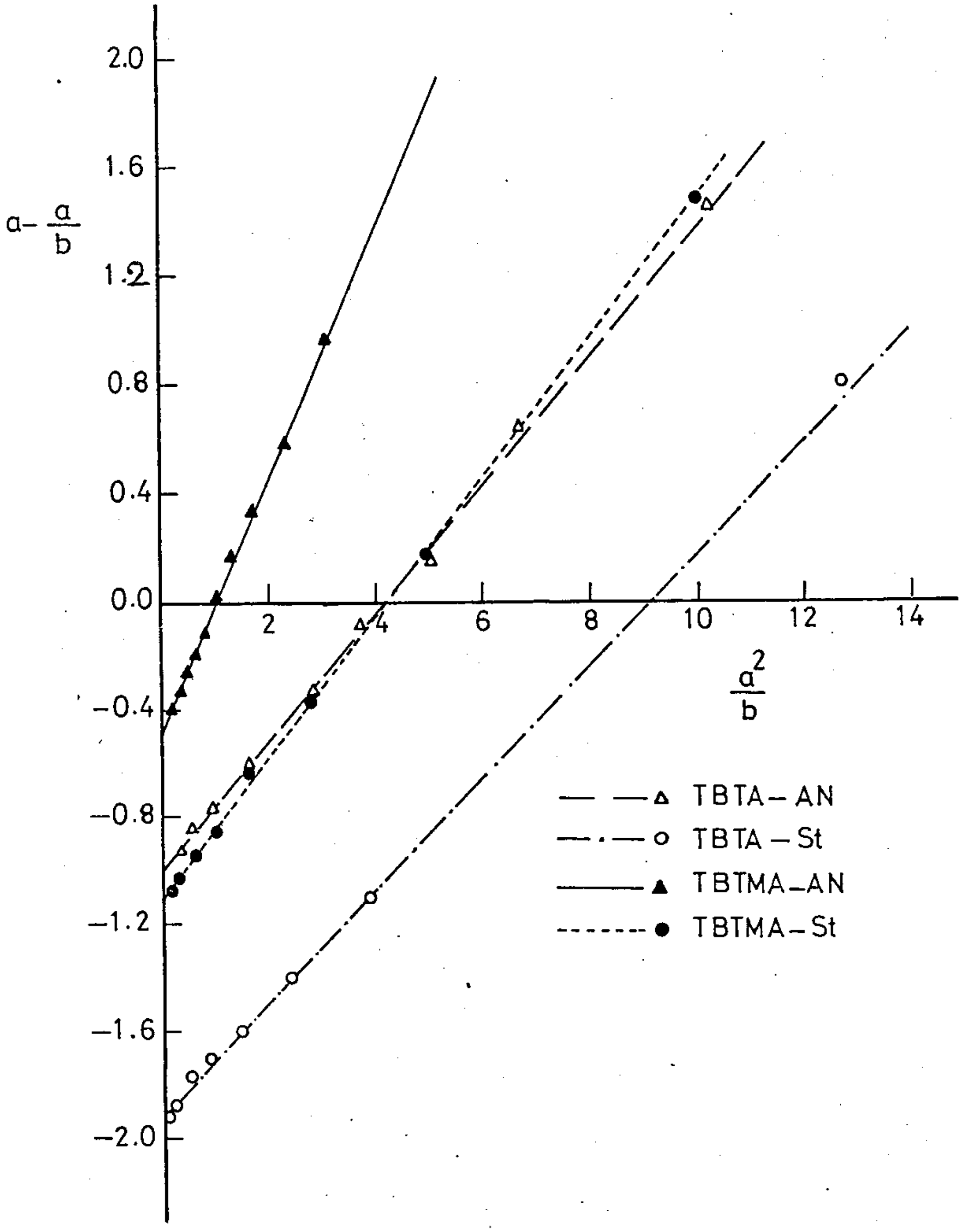


Fig. (22). Fineman−Ross plots for the copolymerization of TBTA-AN, TBTA-St, TBTMA-AN, and TBTMA-St.

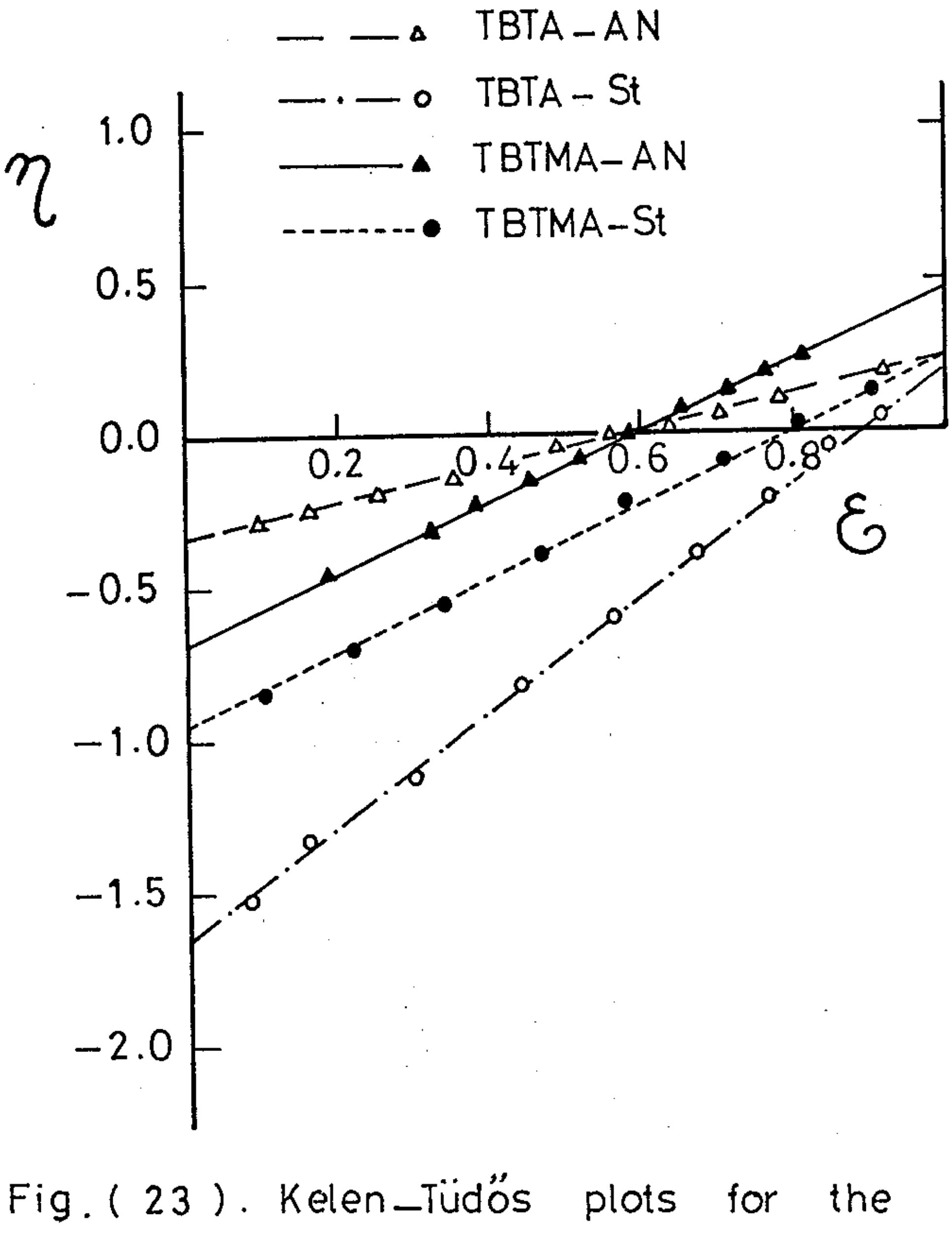


Fig. (23). Kelen–Tüdős plots for the copolymerization of: TBTA-AN, TBTA – St , TBTMA – AN , and TBTMA – St .

The data illustrated in Table (27) show that there is a good agreement between the monomer reactivity ratios calculated by the two methods.

From the reactivity ratios of the four systems for the copolymerization of TBTMA and TBTA with AN and St given in Table (27), it is clear that the copolymers should have random distribution of the monomer units in the copolymer molecules. Table (27) also shows that r_1 and r_2 determined for the copolymerization of TBTMA with AN is less than unity and should have azeotropic copolymerization behaviour. The azeotropic composition of TBTMA-AN system was calculated from the monomer reactivity ratios and was found to be at 49.91:50.02 mole ratio. This data is in agreement with the composition curves (Fig. 24) which shows the relation between F_1 (mole fraction of TBTMA or TBTA in copolymer) versus f_1 (mole fraction of TBTMA or TBTA in comonomer feed). From Fig. (24a), it is clear that the curve crosses the line representing $F_1=f_1$ at 0.50 mole fraction for copolymerization of TBTMA with AN. This point of intersection corresponds to the azeotropic composition yielding homogeneous copolymer regardless of conversion.

The azeotropic comonomer mixture of TBTMA and AN was polymerized, by solution copolymerization in toluene in presence of 1 mole % AIBN at 70°C, to several conversions covering a

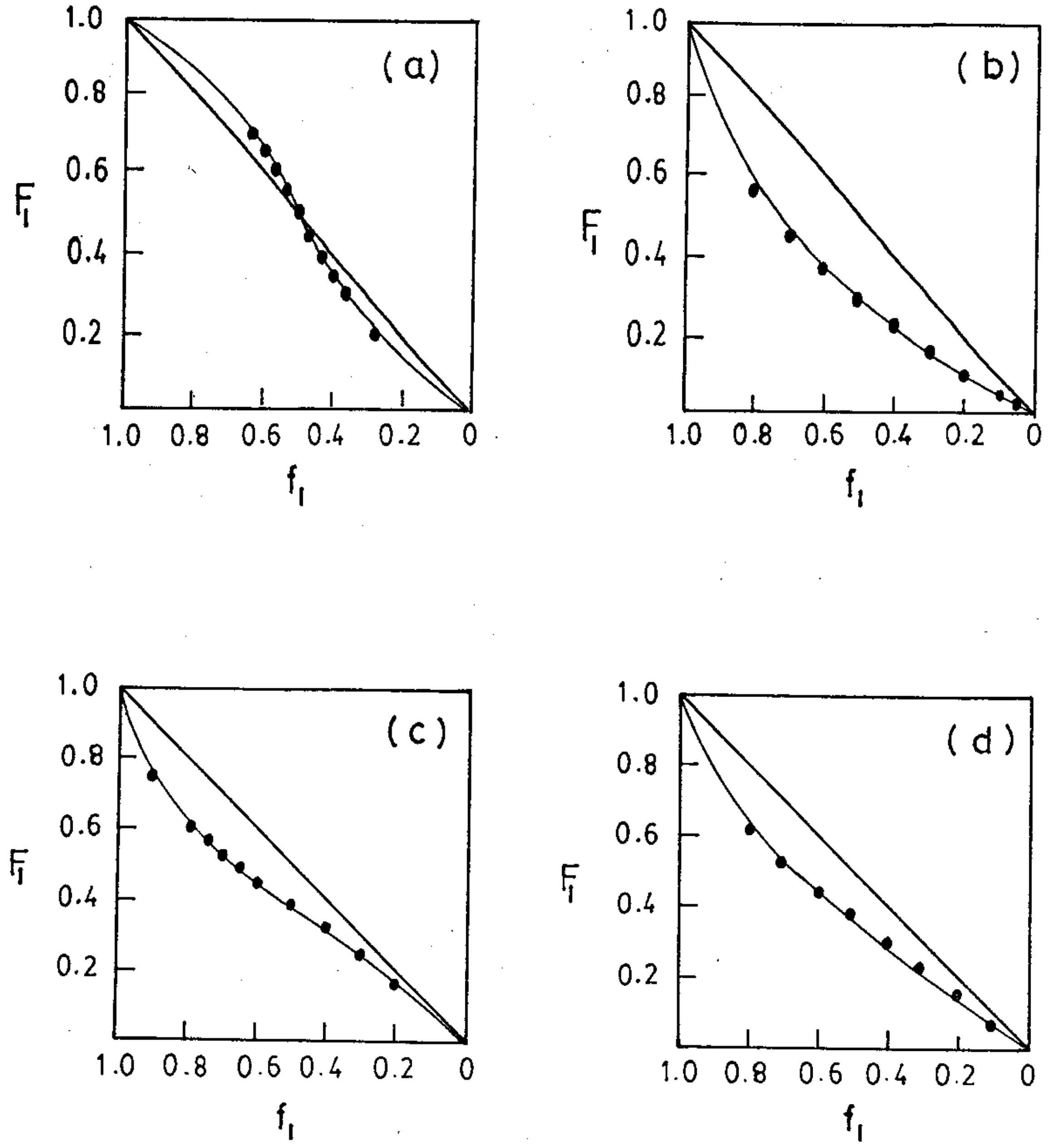


Fig. (24). Composition curves for the copolymerization of : (a) TBTMA-AN , (b) TBTA —St , (c) TBTA-AN , and (d) TBTMA-St where f_1 = mole fraction of M_1 in feed and F_1 = mole fraction of M_1 in copolymer.

wide range. Table (28) illustrates the experimental conditions and the results for the azeotropic copolymerization of TBTMA with AN. Fig. (25) shows the relation between percent conversion versus time for the azeotropic copolymerization of TBTMA-AN. Fig. (26) shows F_1 (mole fraction of TBTMA in copolymer) against % conversion and indicates that the experimental points, calculated from the tin content of each sample, are in good agreement with the line representing the azeotropic composition of TBTMA-AN system. From Table (28) and Fig. (26), it is clear that the azeotropic copolymer composition of TBTMA-AN remains constant up to 90 % conversion, and the tin content of the copolymers gave a mean value of 27.52 % against a calculated value of 27.80 % for the azeotropic composition of TBTMA-AN system.

The sequence distribution of the monomer units at the azeotropic composition of the TBTMA-AN system was calculated from the normograph of Izu and O'Driscoll[61]. Thus, the triad fractions for the azeotropic copolymer of TBTMA-AN was found to be as :

f_{111}	f_{112}	f_{121}	f_{212}
0.0480	0.1069	0.2380	0.2380

Table (28)

Azeotropic copolymerization of TBTMA (M_1)
with AN (M_2)

	Mole fraction	gram
TBTMA	0.4998	18.7425
AN	0.5002	2.6511
AIBN	(1 mole %)	0.1640

Solution polymerization in toluene (3 moles/l, total volume 33.33 ml) at 70°C.

Time (minutes)	Conversion %	Sn %	F_1
30	13.87	26.69	0.4281
50	21.55	27.64	0.4885
70	29.50	27.91	0.5080
100	36.89	27.75	0.4963
120	45.46	26.51	0.4178
150	53.79	27.88	0.5058
180	62.06	27.79	0.4992
240	78.39	27.77	0.4978
290	90.23	27.75	0.4963

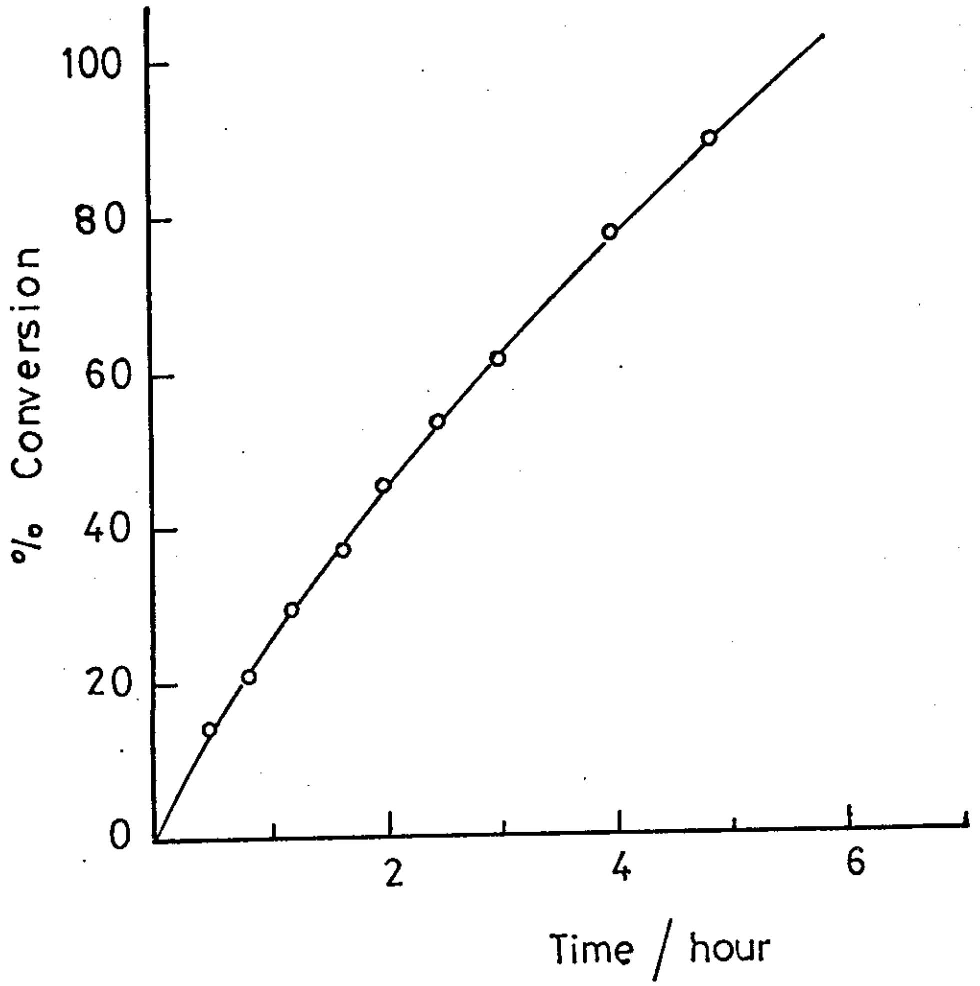


Fig. (25). Variation in percent azeotropic copolymer produced with time for azeotropic copolymerization of TBTMA – AN.

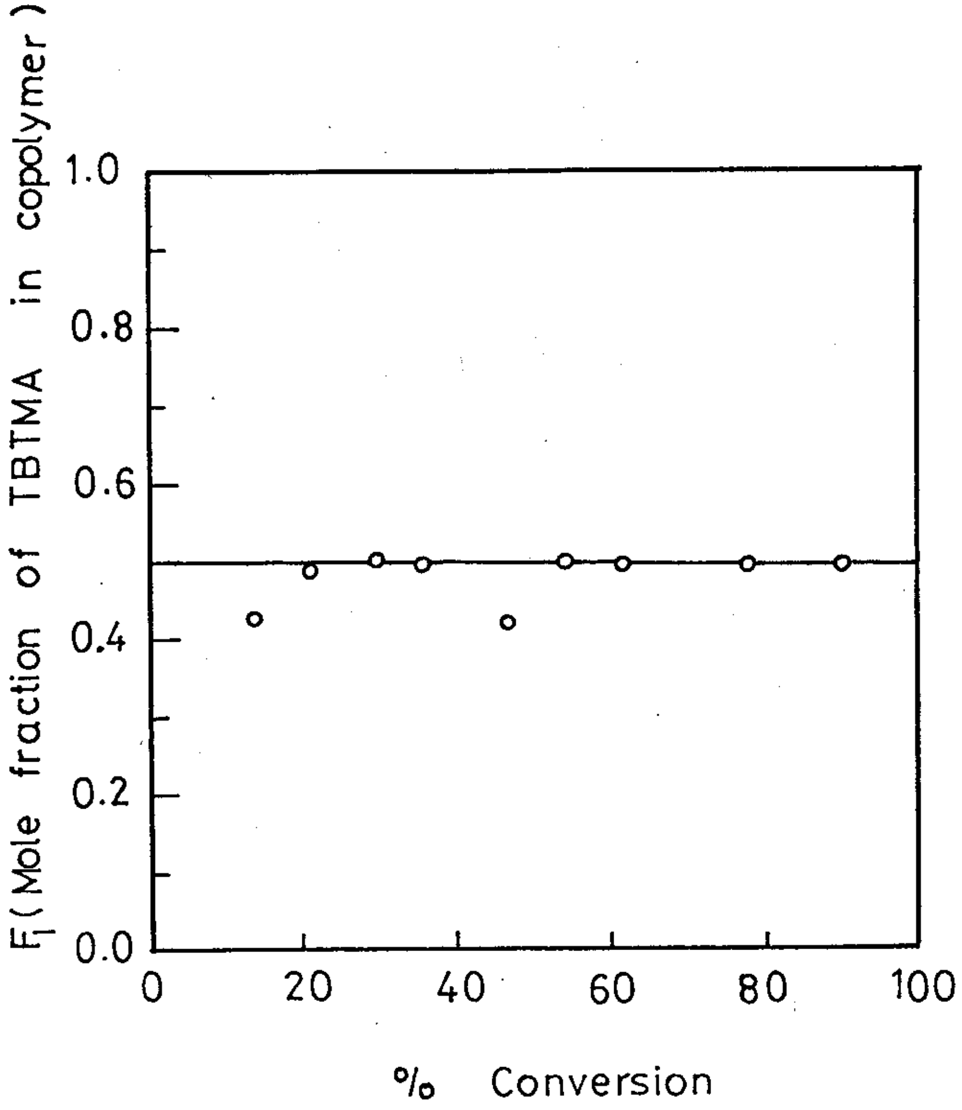


Fig. (26). F_1 as a function of conversion for azeotropic copolymerization of TBTMA – AN.

The structure of the prepared copolymers of TBTMA and TBTA with AN and St was investigated by infrared spectroscopy. The infrared spectra of TBTMA-AN and TBTA-AN copolymers are found to be quite similar and are characterized by the presence of one carboxyl carbonyl band at 1640 cm^{-1} due to the tributyltin carboxylates and a band at 2240 cm^{-1} due to the $-C\equiv N$ group, as shown in Fig. (27) which illustrates the IR spectrum of TBTMA-AN copolymer. Also the IR spectra of TBTMA-St and TBTA-St copolymers are quite similar and were characterized by the presence of two strong bands at 700 cm^{-1} and 750 cm^{-1} due to the mono-substituted benzene ring of styrene and a strong band at 1640 cm^{-1} due to the tributyltin carboxylates and also show bands at 3050-3100 cm^{-1} due to the stretching frequencies of the $=C-H$ bonds. Fig. (28) illustrates the IR spectrum of TBTMA-St copolymer.

Copolymers prepared from the reactions of TBTMA-and TBTA with AN and St are clear, transparent and soluble in several organic solvents even at higher conversions. Films prepared from the azeotropic copolymer of TBTMA-AN exerted some tackiness which might limit its use as binders for antifouling coatings. To improve its film properties, the azeotropic copolymer was prepared at various lower initiator concentrations ranging from 0.25 to 0.05 mole/100 moles monomers, but the

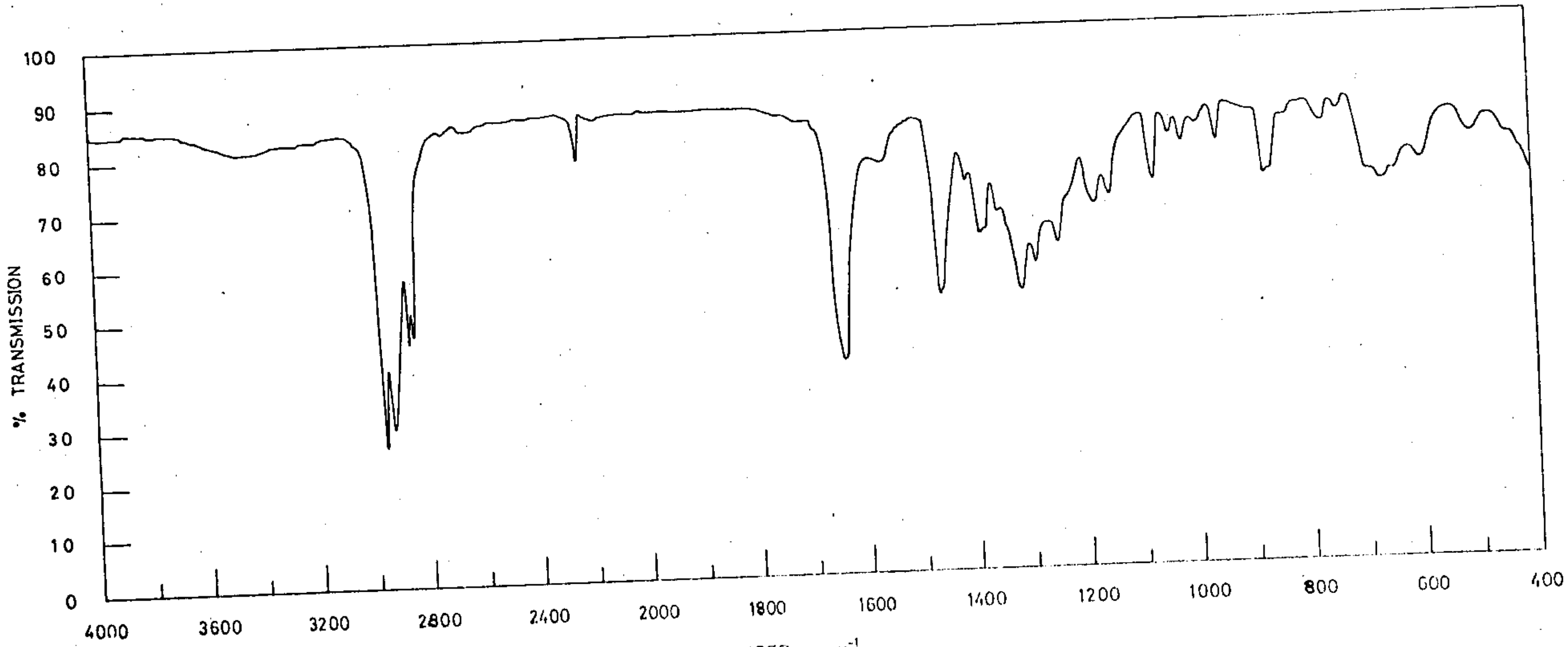


Fig. (27). I.R Spectrum for TBTMA – AN copolymer.

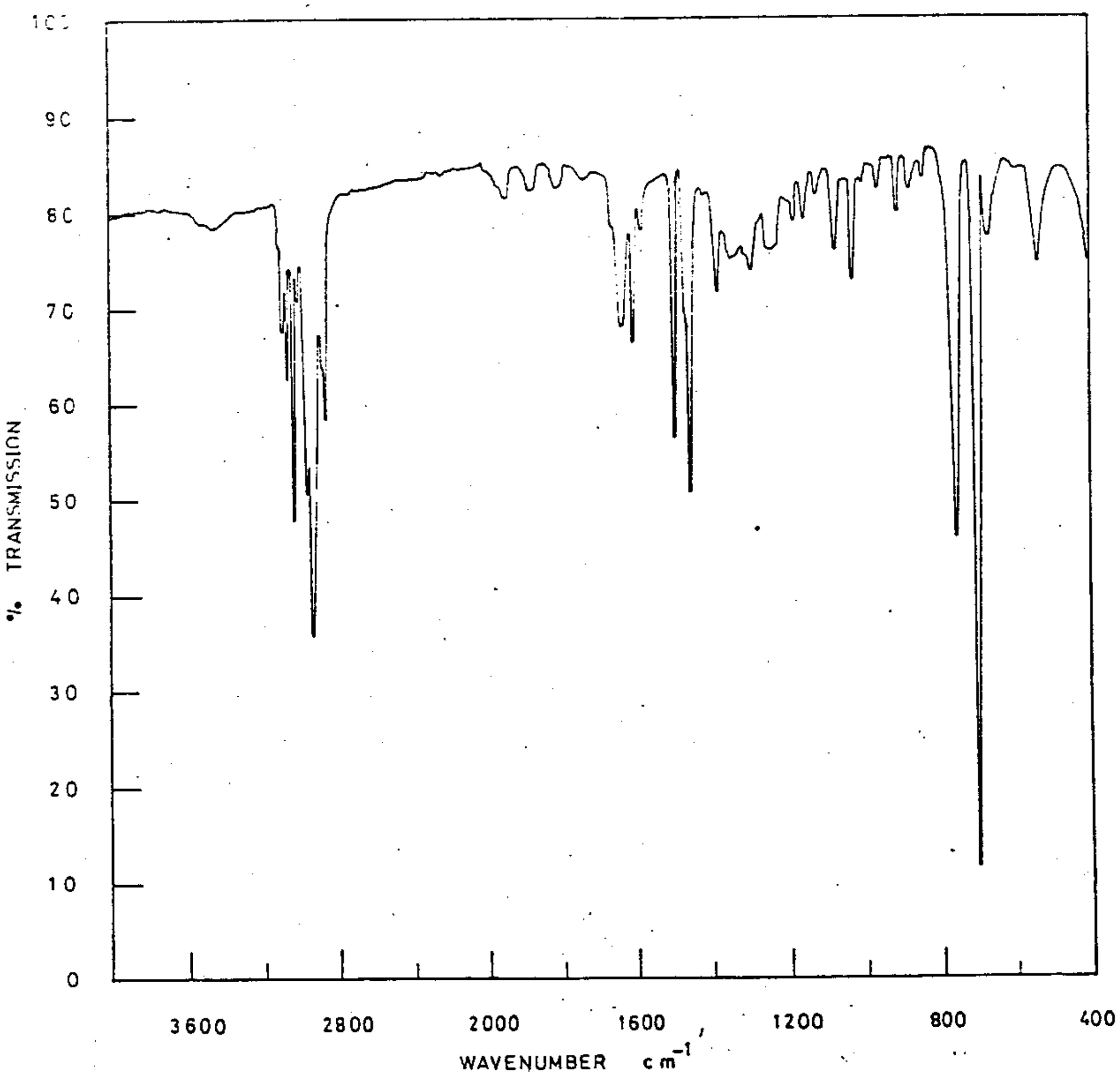


Fig. (28). I.R Spectrum for TBTMA—St copolymer.

tackiness of the films was only a little improved. The viscosity measurements of the azeotropic copolymer (TBTMA-AN) are illustrated in Table (29) which shows that the reduced viscosity of the azeotropic copolymer, 1 % solution in toluene at 30°C, increases with decreasing the initiator concentration. The tackiness of the azeotropic copolymers and the relatively low reduced viscosity values may be due to a chain transfer effect with the solvent (toluene).[62]

Table (29)

Reduced viscosity for the azeotropic copolymerization of TBTMA-AN

Initiator concentration	$\eta_{sp/c}$
1.00 mole %	0.1296
0.25 "	0.1593
0.10 "	0.2113
0.05 "	0.2740

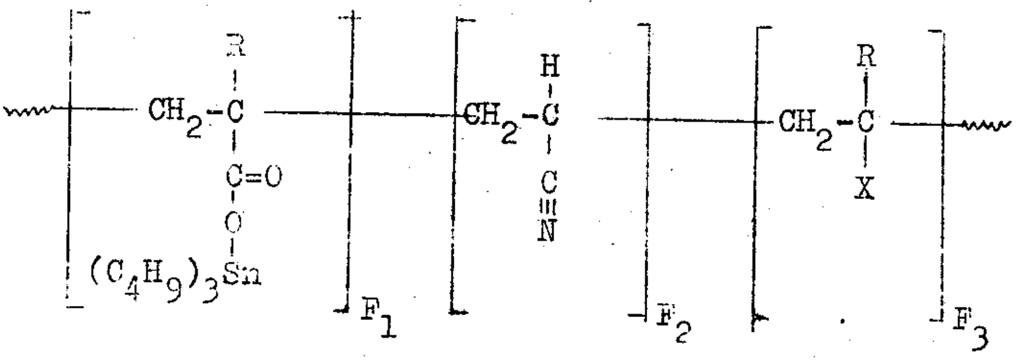
Copolymers prepared from the reaction of styrene with TBTMA and TBTA were clear, transparent solids suitable for film formation.

CHAPTER VIII

Terpolymerization Reactions

Ternary copolymerization reaction of the system involving tri-n-butyltin acrylate or methacrylate and acrylonitrile with the alkyl esters of acrylic or methacrylic acids as well as styrene were prepared by solution polymerization in toluene (3 mole/L) in presence of 1 mole % AIBN initiator at 70°C in the way described before (page 45). Four terpolymer systems involving TBTMA and AN with EA, BA, MMA, or BMA, and also three terpolymer systems involving TBTA and AN with MMA, BMA or St were prepared.

The terpolymers prepared in the present study can be represented by the following general formula as :



$$\sim\left[CH_2-\overset{R}{\underset{\substack{|\\C=O\\|\\O\\|\\(C_4H_9)_3Sn}}{C}}\right]_{F_1}\left[CH_2-\overset{H}{\underset{\substack{|\\C\\\equiv\\N}}{C}}\right]_{F_2}\left[CH_2-\overset{R}{\underset{\substack{|\\X}}{C}}\right]_{F_3}\sim$$

where $R = -H$ or $-CH_3$ and

$X = -COOCH_3, -COOC_2H_5, -COOC_4H_9$ or $-C_6H_5$.

To study the instantaneous terpolymer composition of each system, the terpolymers were polymerized to low conversions (less than 10 %) and the terpolymers produced were analyzed for tin and nitrogen. From the tin content and the nitrogen content of each sample, the terpolymer composition could be calculated. The initially formed terpolymer composition of each system could be calculated by using the terpolymer composition equation in the form proposed by Khan and Horowitz[27] (page 27). The prediction of the terpolymer composition requires the monomer reactivity ratios of the individual two-component systems. Thus, the reactivity ratios used for calculated the terpolymer composition of each system, determined previously from the binary copolymerization reactions of organotin monomers, as well as the literature values for EA-AN, BA-AN, MMA-AN, BMA-AN and St-AN systems, are illustrated in Table (30).

To check the correctness of the reactivity ratios tabulated in Table (30), two feed compositions for each system were selected, polymerized at low conversions, and analyzed for tin and nitrogen. Table (31) illustrates the feed composition and the results of the analysis of the prepared fourteen terpolymer compositions. Also, Table (31) shows good agreement between the found terpolymer composition (based on tin and nitrogen analysis), and the calculated terpolymer composition for each feed, which indicates the correctness of monomer reactivity ratios.

Table (30)

Reactivity ratios in terpolymer systems

M_1-M_2-M_3	Reactivity ratios determined in this work				Reactivity ratios cited from literature		
	r_{12}	r_{21}	r_{13}	r_{31}	r_{23}	r_{32}	Refs.
TBTMA-AN-EA	0.465	0.467	1.259	0.606	1.12	0.93	63
TBTMA-AN-BA	0.465	0.467	0.846	0.572	1.003	1.005	64
TBTMA-AN-MMA	0.465	0.467	0.789	1.004	0.15	1.20	65
TBTMA-AN-BMA	0.465	0.567	0.623	0.646	0.31	1.08	66
TBTA-AN-MMA	0.243	1.008	0.401	2.199	0.15	1.20	65
TBTA-AN-BMA	0.243	1.008	0.196	1.661	0.31	1.08	66
TBTA-AN-St	0.243	1.008	0.213	1.91	0.03	0.52	67

Table (31)

Terpolymer compositions using tin and nitrogen analyses

Exp. No.	M_1 M_2 M_3	Feed Composition (Mole %)	Sn %	N %	Terpolymer composition (Mole %)	
					Found	Calculated
Ia	TBTMA	19.97	21.65	4.48	27.98	27.87
	AN	50.07			49.23	50.92
	EA	29.96			22.80	21.21
Ib	TBTMA	52.11	27.83	2.15	54.51	53.63
	AN	28.67			35.78	34.59
	EA	19.22			9.71	11.78
IIa	TBTMA	19.95	19.70	3.16	27.86	27.37
	AN	40.03			37.99	39.78
	BA	40.02			34.14	32.95
IIb	TBTMA	39.17	25.87	2.74	45.64	43.34
	AN	41.53			41.08	42.34
	BA	19.30			13.27	14.32
IIIa	TBTMA	19.95	16.19	3.88	17.99	17.32
	AN	50.02			36.63	38.06
	MMA	30.03			45.37	44.72
IIIb	TBTMA	29.93	20.23	2.97	26.89	25.18
	AN	40.10			33.54	33.36
	MMA	29.97			39.55	41.46

Table (31), continued.

Exp. No.	M_1 M_2 M_3	Feed composition (mole %)	Sn %	N %	Terpolymer composition (mole %)	
					Found	calculated
IVa	TBTMA	20.00	18.71	4.45	24.36	23.24
	AN	60.35			49.23	48.96
	BMA	19.65			26.39	27.80
IVb	TBTMA	30.03	19.69	2.75	29.77	30.88
	AN	39.94			35.32	34.31
	BMA	30.03			34.90	34.81
Va	TBTA	19.64	10.8	3.71	10.24	8.87
	AN	39.90			29.86	32.65
	MMA	40.46			59.89	58.48
Vb	TBTA	61.90	24.10	2.40	36.69	36.56
	AN	23.48			31.06	32.11
	MMA	14.62			32.25	31.33
VIa	TBTA	29.99	13.30	3.00	16.77	15.54
	AN	40.50			32.15	32.74
	BMA	29.51			51.07	51.72
VIb	TBTA	55.21	17.51	1.74	26.50	27.09
	AN	24.90			22.45	23.37
	BMA	19.89			51.05	49.54
VIIa	TBTA	20.13	8.26	3.25	6.67	7.10
	AN	20.34			27.68	25.85
	St	59.53			66.64	67.06
VIIb	TBTA	39.22	12.91	4.60	12.68	11.91
	AN	40.36			38.44	40.11
	St	20.42			48.86	47.98

It is well known that molecular heterogenity has a direct effect on the physical properties of polymers, and the co- or terpolymer composition varies with conversion except for the systems having azeotropic behaviour. On the basis of the determined reactivity ratios determined from the binary copolymerization reactions of TBTMA and TBTA (Tables 7, 13, 20 and 27) and the literature values, it was found that any terpolymer system involving organotin moiety with azeotropic composition could be prepared. Thus, terpolymer systems illustrated in Table (31) with feed compositions Ia-VIIa, were polymerized to different extents of conversion as shown in Figs. (29 and 30) which illustrate the percent conversion as a function of time for each system. Then, each sample at each extent of conversion was analyzed for its tin and nitrogen contents, from which the terpolymer composition of each sample was calculated.

Tables (32-38), illustrate the experimental conditions and results of the terpolymerization reactions.

Prediction of both the instantaneous and average terpolymer composition at each extent of conversion was calculated for each terpolymer system on the basis of the feed composition and the monomer reactivity ratios of each system tabulated in **Table** (30) by integration of the terpolymer composition

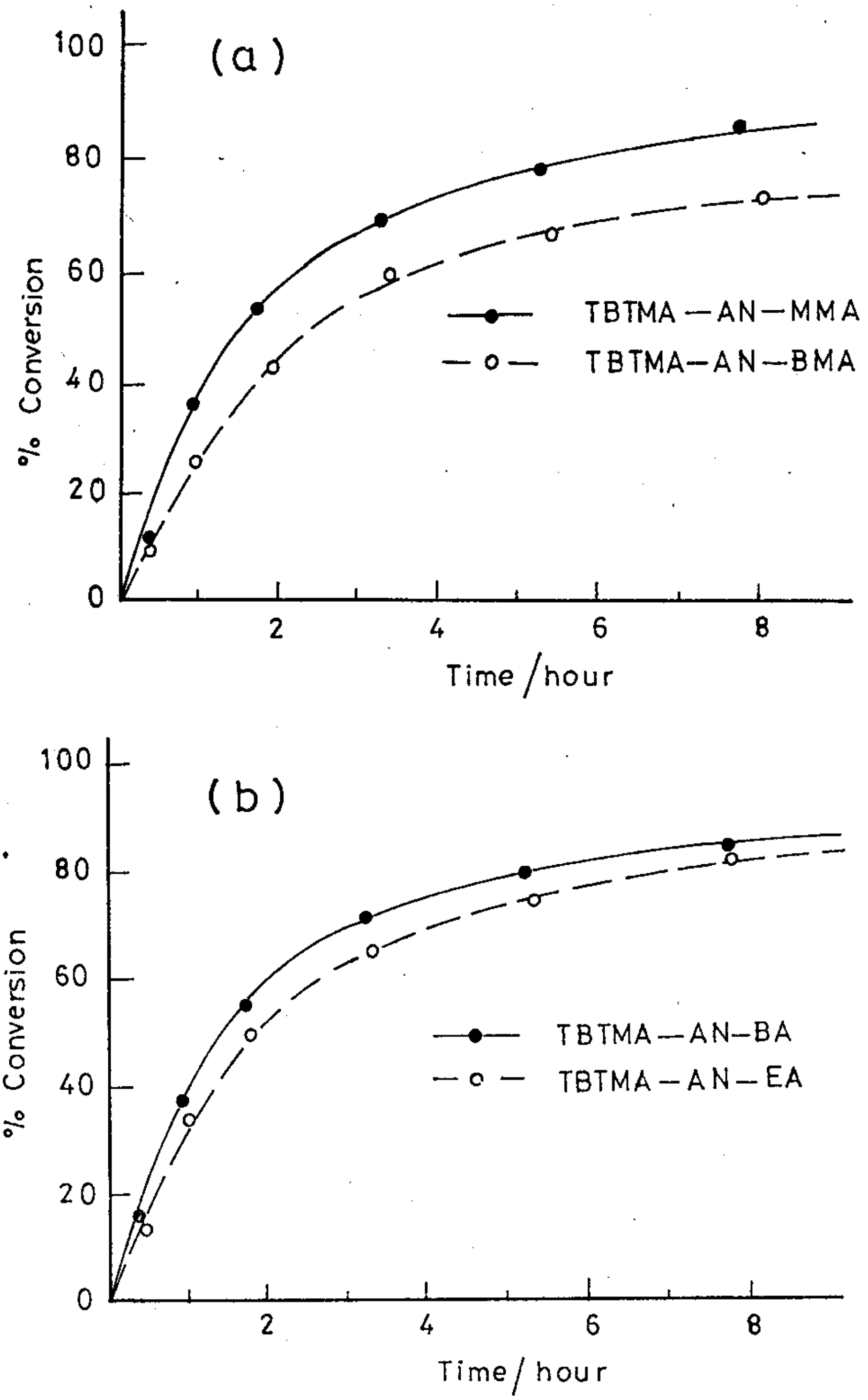


Fig. (29). Variation in percent terpolymers produced with time for: (a) TBTMA-AN-MMA and TBTMA-AN-BMA; and (b) TBTMA-AN-EA and TBTMA-AN-BA.

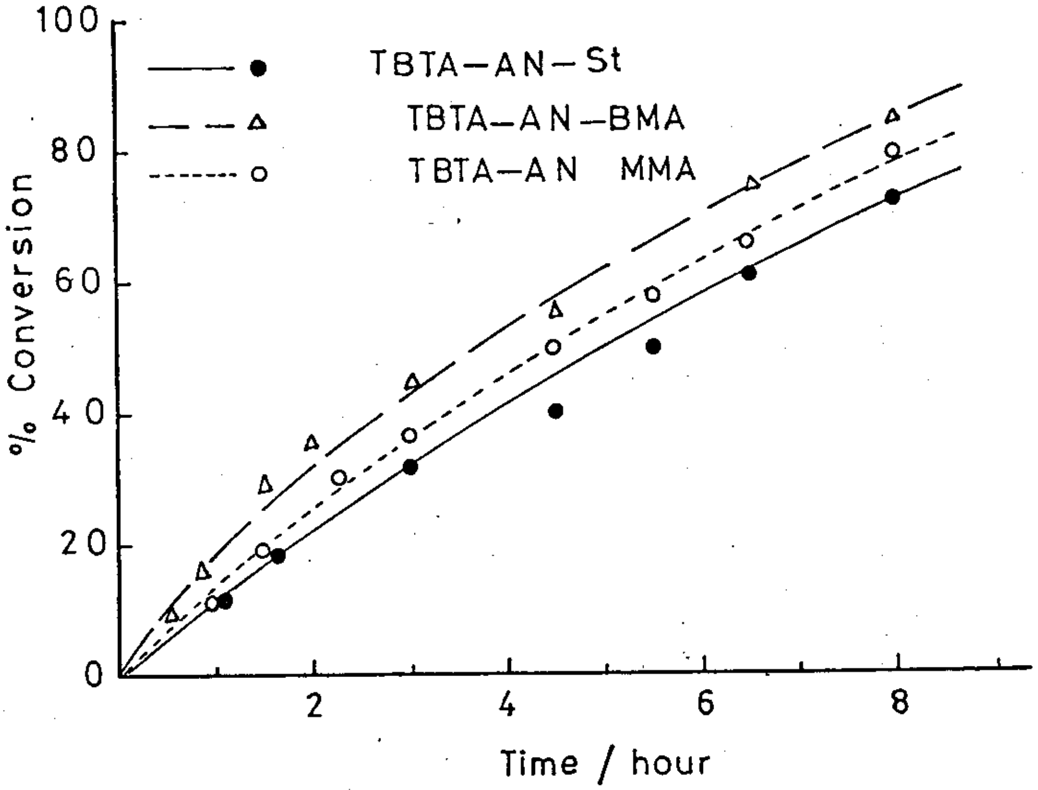


Fig. (30). Variation in percent terpolymers produced with time for : TBTA-AN–St, TBTA–AN–BMA and TBTA–AN–MMA.

equation proposed by Khan and Horowitz[27] (page 27), assuming that the terpolymer composition is constant within 10 % intervals. The variations of the calculated instantaneous terpolymer composition (Mole %) and average terpolymer composition (wt. %) as a function of conversion for the seven terpolymer systems studied are illustrated in Figs. (31-37).

From the conversion-composition curves of TBTMA-AN-EA and TBTMA-AN-BA systems (Figs. 31 and 32), it is clear that TBTMA is completely consumed at 95 % conversion in the both systems, after which a copolymers of AN-EA and AN-BA are formed, and that AN content of the two terpolymers remain almost constant up to 90 % conversion.

From Figs. (33 and 34) which illustrate the conversion-composition curves for TBTMA-AN-MMA and TBTMA-AN-BMA systems, it is clear that both MMA and BMA decrease continuously with conversion and were completely consumed at 86 % and 90 % conversions, respectively. Also, TBTMA in the both systems was completely disappeared at 95 % conversion, while acrylonitrile content increase continuously with conversion for both systems.

Figs. (35 and 36) illustrate the conversion-composition curves for TBTA-AN-MMA and TBTA-AN-BMA systems, which show that MMA and BMA contents were decreased continuously with conversion and were completely disappeared at 85 % and at 77 % conversions, respectively. Also AN was consumed at 97 % and 96 % conversions, respectively, while TBTA content for both systems increase continuously up to 100 % conversion.

From Fig. (37), which illustrates the conversion-composition curve for TBTA-AN-St system, it is clear that both AN and St decrease continuously with conversion and were consumed at 93 % and at 95 % conversions, after which a homopolymer of TBTA was only formed.

Tables (32-38) indicate that the results obtained from the analysis of the seven terpolymer systems studied at different levels of conversions, calculated as average terpolymer composition (wt. %) are in good agreement with the predicted curves as illustrated in Figs. (31-37). Also, from Figs. (31-37), it is clear that terpolymerization of the systems studied give a wide spectrum of polymer compositions with conversion and obviously when uniformity of polymer composition is desired, proper amounts of the more reactive monomers must be continuously added.

Terpolymers obtained from the seven systems studied were pale yellowish rubbery products, except terpolymers containing MMA or St which were solids, and soluble in organic solvents even at higher conversions.

The structure of the prepared terpolymers was investigated by IR spectroscopy and were found to show as expected two strong bands at 1640 cm^{-1} and at 1720 cm^{-1} due to the carboxylate carbonyl groups and the carbonyl groups of the alkyl acrylates or methacrylates, respectively, and also the bands due to the $-C\equiv N$ of acrylonitrile appeared at 2240 cm^{-1}. Fig. (38) illustrates the IR spectra for the TBTMA-AN-BMA and TBTA-AN-St systems, as examples for the prepared terpolymers.

Table (32)

Average terpolymer composition for terpolymerization of TBTMA, AN and EA

	Mole percent	gram
EA :	29.96	5.992
TBTMA :	19.97	14.9775
AN :	50.07	5.3074
AIBN :	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°C.

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt.%		
				TBTMA	AN	EA
0.41	12.7	21.65	4.48	68.22	16.96	14.82
0.916	34.1	21.48	4.68	67.68	17.71	14.61
1.75	49.4	21.12	4.80	66.55	18.17	15.28
3.25	65.4	20.38	4.83	64.22	18.28	17.50
5.25	73.9	20.31	4.94	64.00	18.7	17.30
7.55	82.1	19.16	4.89	60.37	18.51	21.12

Table (33)

Average terpolymer composition for terpolymerization of TBTMA, AN and BA

		Mole percent	gram
BA	:	40.02	10.2451
TBTMA	:	19.95	14.9625
AN	:	40.03	4.2432
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt %.		
				TBTMA	AN	BA
0.41	15.80	20.70	3.16	65.23	11.96	22.81
0.916	37.80	20.02	3.14	63.08	11.88	25.04
1.75	54.80	18.92	3.33	59.62	12.60	27.78
3.25	71.00	18.22	3.28	57.41	12.41	30.18
5.25	79.30	17.76	3.53	55.96	13.36	30.68
7.75	84.00	17.38	3.65	54.76	13.81	31.43

Table (34)

Average terpolymer composition for terpolymerization of TBTMA, AN and MMA

		Mole percent	gram
MMA	:	30.03	6.0060
TBTMA	:	19.95	14.9625
AN	:	50.02	5.3021
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°C

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt. %		
				TBTMA	AN	MMA
0.41	12.18	16.90	3.88	51.02	14.68	34.29
0.916	37.40	16.32	3.95	51.42	14.95	33.62
1.75	54.10	16.43	4.33	51.77	16.39	31.83
3.25	70.50	16.82	4.48	53.00	16.96	30.04
5.25	78.40	17.80	4.58	56.09	17.33	26.57
7?75	85.40	18.00	4.58	56.72	17.33	25.94

Table (35)

Average terpolymer composition for terpolymerization of TBTMA, AN and BMA

		Mole percent	gram
BMA	:	19.65	5.5806
TBTMA	:	20.00	15.0000
AN	:	60.35	6.3971
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°C

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt. %		
				TBTMA	AN	BMA
0.41	9.76	18.71	4.45	58.96	16.84	24.20
0.91	25.80	18.83	4.45	59.33	16.84	23.83
1.91	43.50	18.71	4.23	58.96	16.01	25.03
3.41	59.90	18.23	4.38	57.40	16.58	26.02
5.41	66.60	18.38	4.88	57.92	18.47	23.61
8.00	73.30	18.40	4.96	57.98	18.72	23.30

Table (36)

Average terpolymer composition for terpolymerization of TBTA, AN and MMA

		Mole percent	gram
MMA	:	40.46	8.0920
TBTA	:	19.64	14.1801
AN	:	39.90	4.2294
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/1, total volume 66.67) at 70°C.

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt. %		
				TBTA	AN	MMA
1.0	10.9	10.82	3.71	32.81	14.04	53.15
1.5	18.9	10.85	4.03	32.91	15.25	51.84
2.25	30.7	10.85	3.90	32.91	14.70	52.39
3.0	36.8	11.28	4.11	34.21	15.50	50.29
4.5	49.5	11.28	4.11	34.21	15.50	50.29
5.5	57.5	11.89	3.93	36.07	14.80	49.13
6.5	65.5	12.50	3.90	37.90	14.70	47.40
8.0	79.5	13.50	4.00	40.90	15.14	43.96

Table (37)

Average terpolymer composition for terpolymerization of TBTA, AN and BMA

		Mole percent	gram
BMA	:	29.51	8.3808
TBTA	:	29.99	21.6528
AN	:	40.50	4.293
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°C.

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt. %		
				TBTA	AN	BMA
0.5	9.50	13.30	3.00	40.34	11.35	48.31
0.83	16.00	13.30	3.00	40.34	11.35	48.31
1.5	29.50	13.80	3.10	41.86	11.73	46.41
2.0	36.80	14.30	3.19	43.38	12.07	44.55
3.0	44.50	14.80	3.15	44.80	11.92	43.28
4.5	55.00	15.09	3.26	45.77	12.34	41.89
6.5	74.00	16.47	3.28	49.90	12.41	37.69
8.0	85.00	17.20	3.30	52.17	12.49	35.34

Table (38)

Average terpolymer composition for terpolymerization of TBTA, AN and St

		Mole percent	gram
St	:	59.53	12.3822
TBTA	:	20.13	14.5339
AN	:	20.34	2.1560
AIBN	:	(1 mole %)	0.3280

Solution polymerization in toluene (3 mole/l, total volume 66.67 ml) at 70°C.

Time (hour)	Conversion %	Sn %	N %	Terpolymer composition wt. %		
				TBTA	AN	St
1.08	11.17	8.26	3.25	25.05	12.30	62.65
1.66	18.31	8.30	3.20	25.17	12.11	62.72
3.00	31.60	9.04	3.19	27.42	12.07	60.51
4.50	39.90	8.73	3.15	26.48	11.92	61.60
5.50	49.30	9.60	3.00	29.12	11.35	59.53
6.50	60.90	10.09	3.00	30.60	11.35	58.05
8.00	72.50	10.90	2.90	33.06	10.97	55.97
9.00	85.00	11.98	2.85	36.34	10.78	52.88

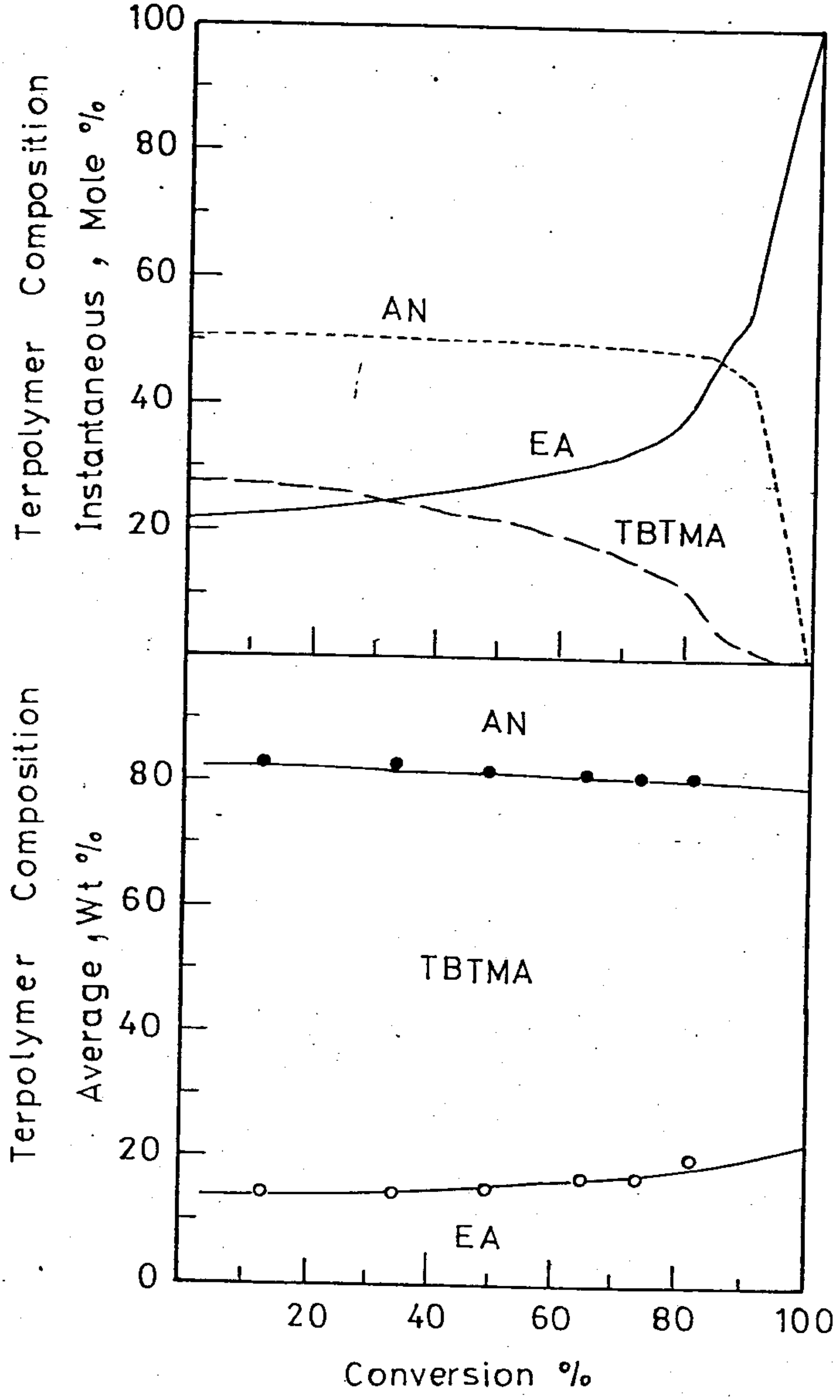


Fig. (31). Variation of instantaneos and average terpolymer composition with conversion for TBTMA-AN-EA, feed charge Ia, lines represent calculated values and (o & ●) from nitrogen and tin analyses.

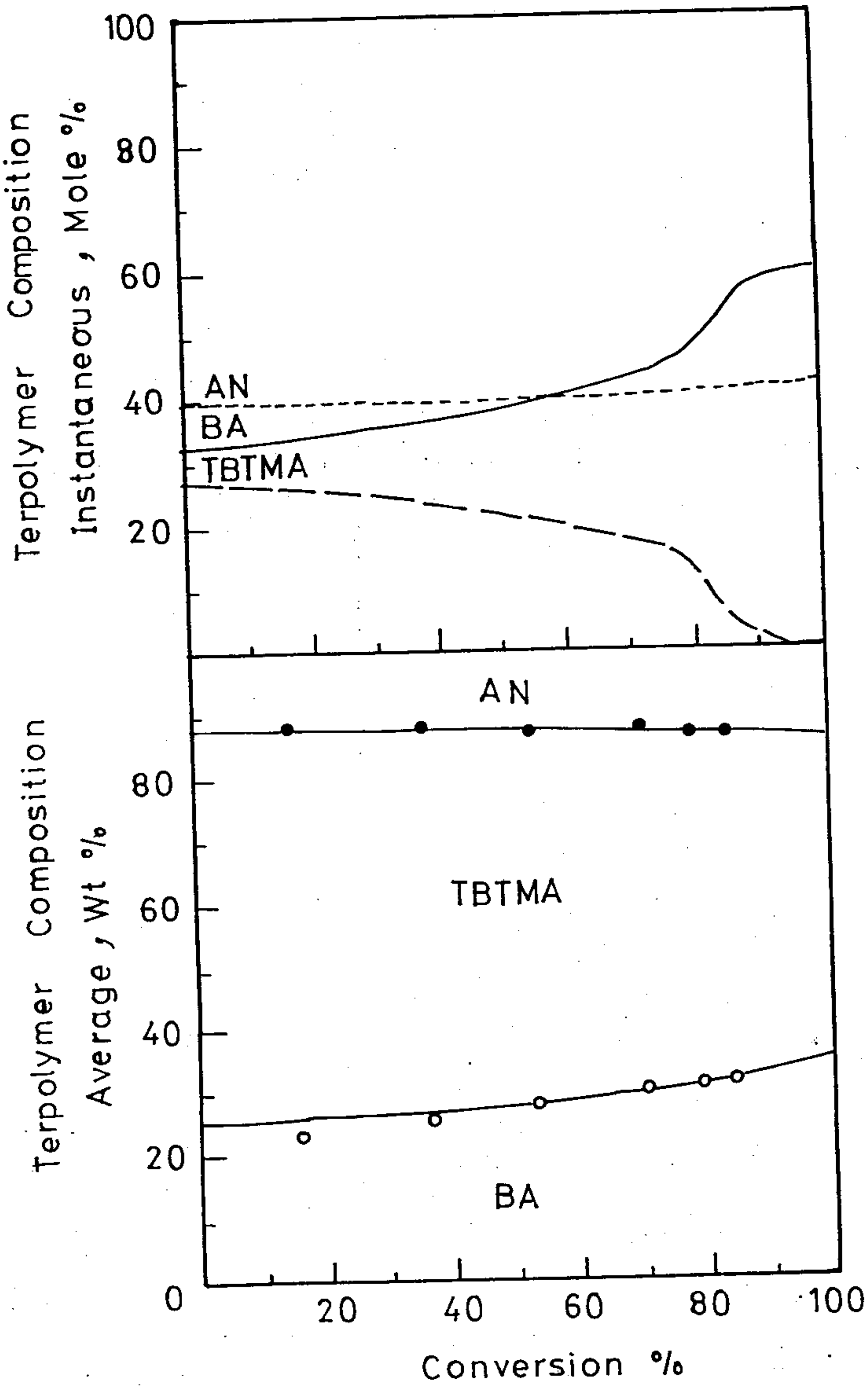


Fig. (32). Variation of instantaneous and average terpolymer composition with conversion for TBTMA-AN-BA, feed charge IIa, lines represent calculated values and (o & ●) from nitrogen and tin analyses.

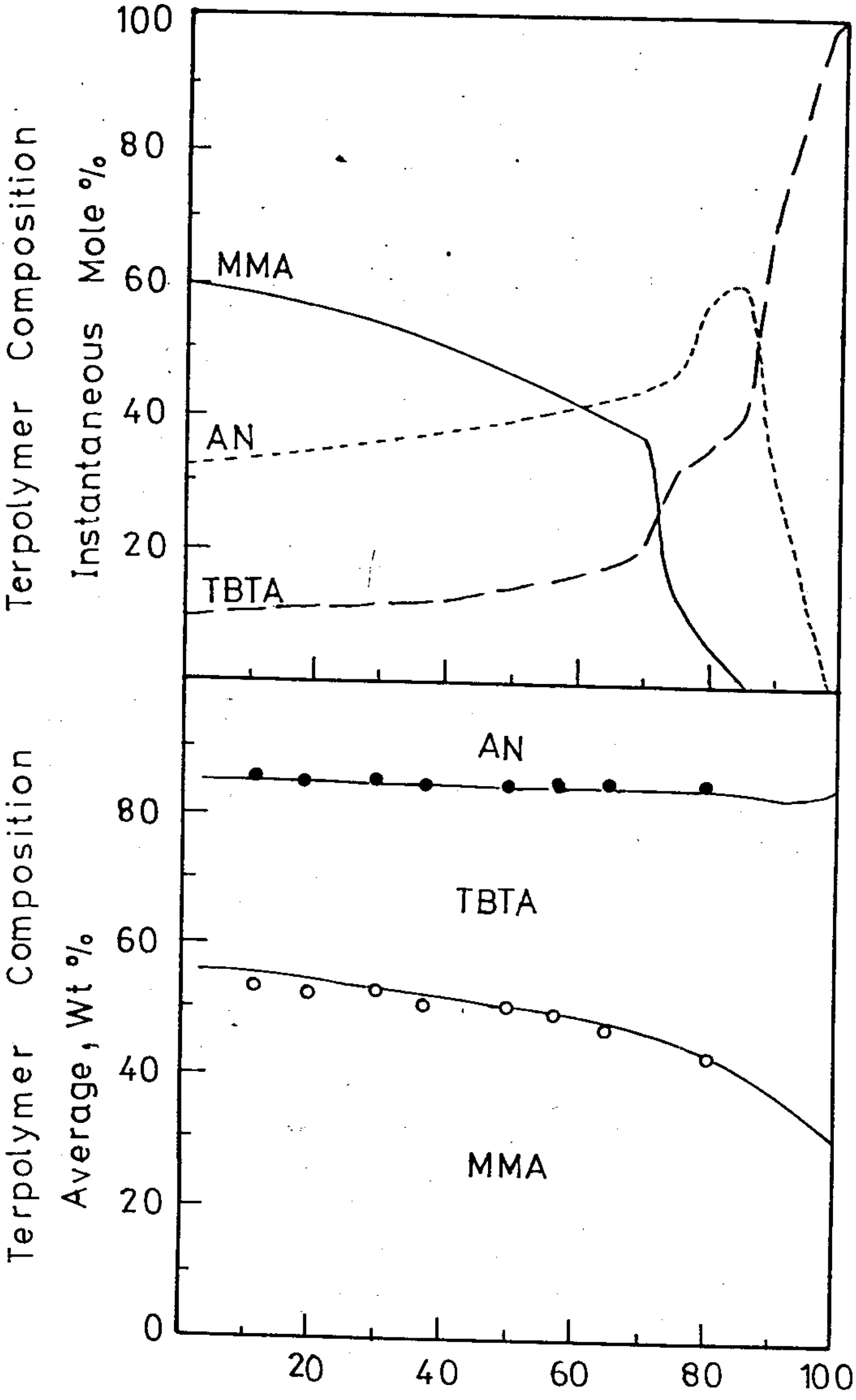


Fig. (35). Variation of instantaneous and average terpolymer composition with conversion for TBTA-AN-MMA, feed charge Va, lines represent calculated values and (o & ●) from nitrogen and tin analyses.

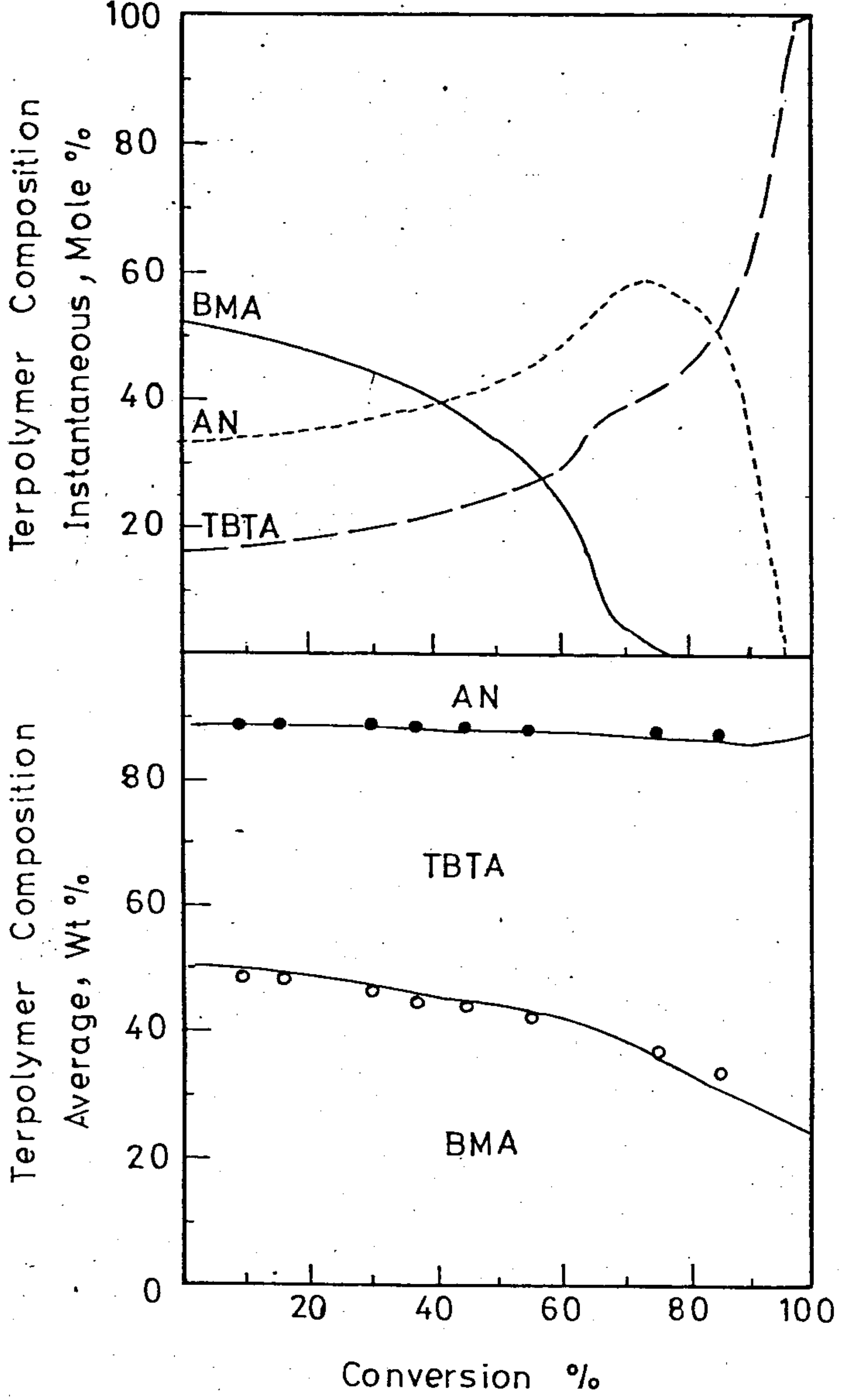


Fig. (36). Variation of instantaneous and average terpolymer composition with conversion for TBTA-AN-BMA, feed charge VIa, lines represent calculated values and (o&●) from nitrogen and tin analyses.

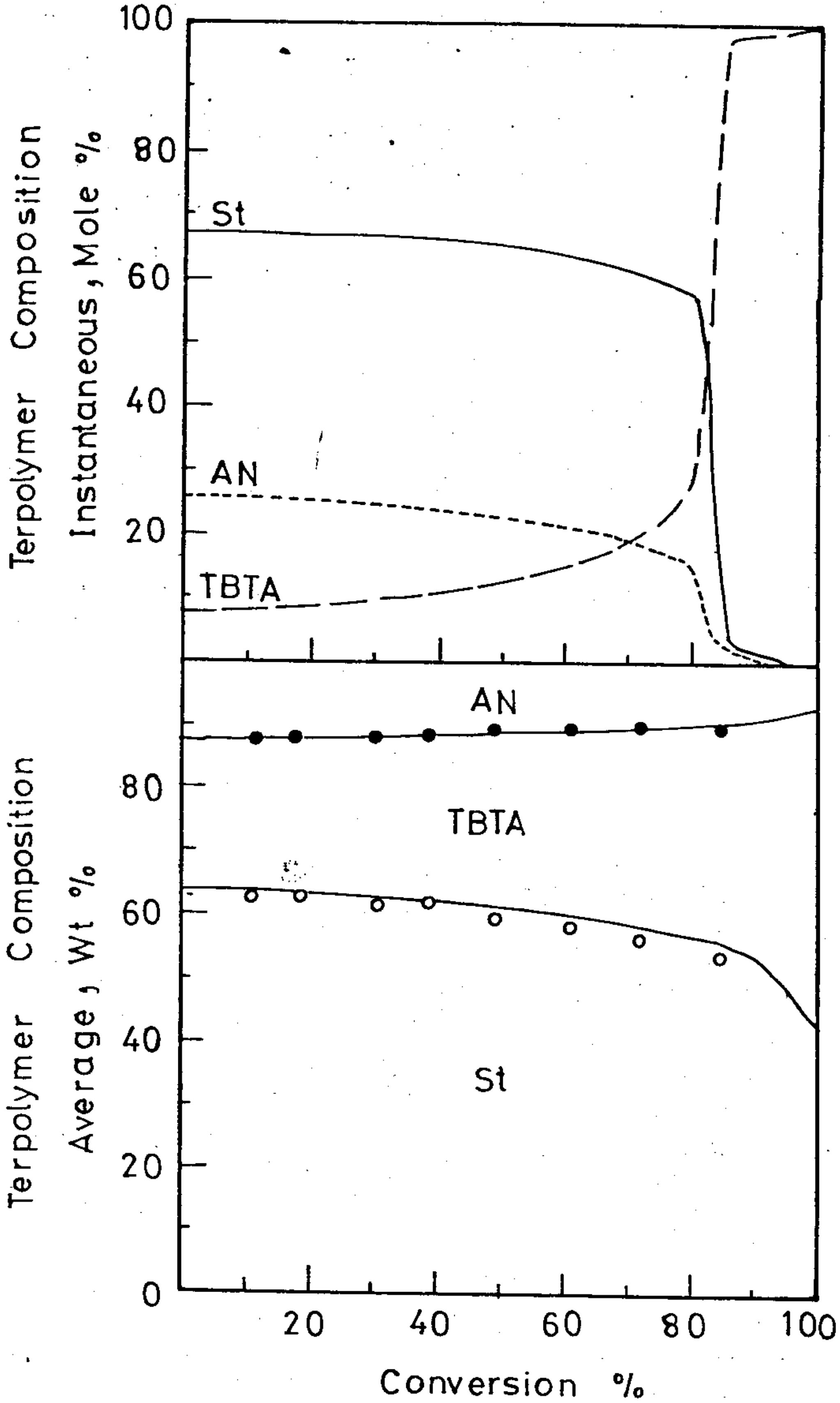


Fig. (37). Variation of instantaneous and average terpolymer composition with conversion for TBTA-AN-St, feed charge VIIa, lines represent calculated values and (o & ●) from nitrogen and tin analyses.

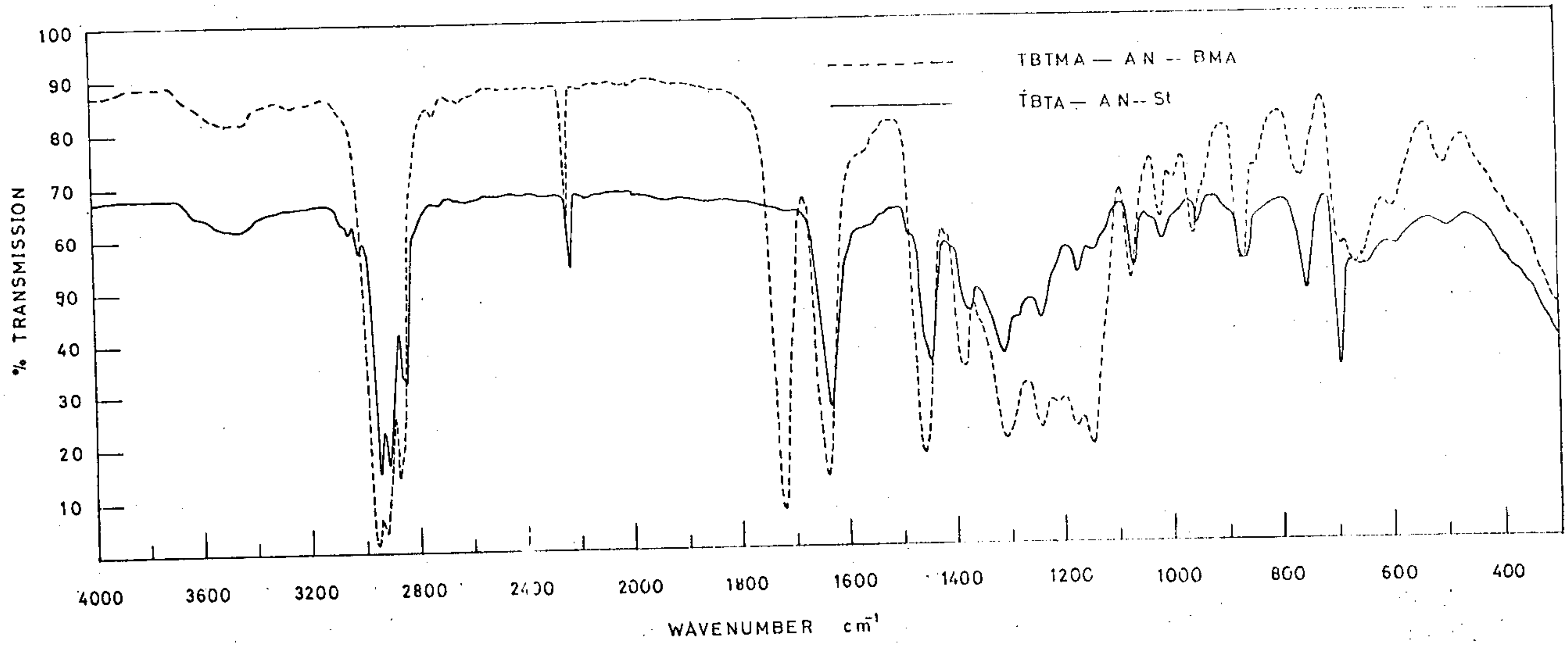


Fig. (38). I.R Spectra for TBTMA-AN-BMA and TBTA-AN-St terpolymers.

CHAPTER IX

Preparation and Properties of Some Film-Forming Organotin Polymers

A set of co- and terpolymer compositions were selected, according to the behaviour of different monomers in co- and terpolymerization reactions which were described in chapters IV-VIII. The aim was to prepare co- and terpolymers having suitable film properties. Three copolymer and eight terpolymers were prepared according to the method described in page (45) at high conversions of about 90 %.

The films were prepared by pouring the solution of co- and terpolymers on glass, tin, and PVC plates to obtain suitable films for testing and evaluation. Film hardness, cold and hot water resistance, synthetic sea water resistance, impact strength and elasticity were performed according to the specifications detailed in Chapter II. The experimental conditions and results are summarized in Tables (39-49).

Table (39)

Preparation of tri-n-butyltin methacrylate-methyl methacrylate copolymer

TBTMA : MMA = 30:70 mole %

Reaction time = 5 hours

Conversion = 88 %

Tin content = 18.72%(calc. 19.56 %, at 100 % conversion).

Film properties of TBTMA-MMA copolymer

Test	Result
Thickness	100 µm
Hardness (pendulum)	101.3 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 0.25 foot

Table (40)

Preparation of tri-n-butyltin methacrylate-methyl methacrylate-n-butyl methacrylate terpolymer

TBTMA:MMA:BMA = 30:50:20 mole %
Reaction time = 5 hours
Conversion = 97 %
Tin content = 18.59%(calc. 18.70% at 100 conversion).

Film properties of TBTMA-MMA-BMA terpolymer

Test	Result
Thickness	95 µm
Hardness (pendulum)	81.67 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 0.25 foot

Table (41)

Preparation of tri-n-butyltin methacrylate-methyl methacrylate-acrylonitrile terpolymer

TBTMA:MMA:AN = 30:50:20 mole %

Reaction time = 5 hours

Conversion = 82 %

Tin content = 19.98%(20.62% calc., at 100 % conversion)

Film properties of TBTMA-MMA-AN terpolymer

Test	Result
Thickness	85 µm
Hardness (pendulum)	95.67 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	damaged
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 0.25 foot

Table (42)

Preparation of tri-n-butyltin methacrylate-methyl methacrylate-tri-n-butyltin acrylate terpolymer

TBTMA:MMA:TBTA = 20:70:10 mole %
Reaction time = 5 hours
Conversion ≃ 96 %
Tin content = 18.94%(calc. 19.71%,at 100 % conversion).

Film properties of TBTMA-MMA-TBTA terpolymer

Test	Result
Thickness	120 µm
Hardness (pendulum)	97.9 seconds
Adhesion	fair
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 0.25 foot

Table (43)

Preparation of tri-n-butyltin acrylate-methyl methacrylate copolymer

TBTA:MMA = 30:70 mole %

Reaction time = 6 hours

Conversion = 96 %

Tin content = 19.14%(Calc. 20.02%, at 100 % conversion)

Film properties of TBTA-MMA copolymer

Test	Result
Thickness	140 µm
Hardness (pendulum)	31.7 seconds
Adhesion	fair
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 0.25 foot

Table (44)

Preparation of tri-n-butyltin acrylate-methyl methacrylate-acrylonitrile terpolymer

TBTA:MMA:AN = 30:50:20 mole %
Reaction time= 6 hours
Conversion = 90 %
Tin content = 19.92%(Calc. 21.14%, at 100 % conversion)

Film properties of TBTA-MMA-AN terpolymer

Test	Result
Thickness	105 µm
Hardness (pendulum)	29.5 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	damaged
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1.3 foot

Table (45)

Preparation of tri-n-butyltin acrylate-methyl methacrylate-n-butyl methacrylate terpolymer

TBTA:MMA:BMA = 30:50:20 mole %

Reaction time = 6 hours

Conversion = 97 %

Tin content = 19.04%(Calc. 19.12%,at 100 % conversion)

Film properties of TBTA-MMA-BMA terpolymer

Test	Result
Thickness	95 µm
Hardness (pendulum)	17 seconds
Adhesion	fair
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1.25 foot

Table (46)

Preparation of tri-n-butyltin methacrylate-styrene copolymer

TBTMA:St = 40:60 mole %

Reaction time = 10 hours

Conversion = 70 %

Tin content = 20.85 % (Calc. 22.41%, at 100 % conversion)

Film properties of TBTMA-St copolymer

Test	Result
Thickness	90 µm
Hardness (pendulum)	1.73 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1.25 foot

Table (47)

Preparation of tri-n-butyltin methacrylate-styrene-n-butyl methacrylate terpolymer

TBTMA:St:BMA = 40:40:20 mole %

Reaction time= 10 hours

Conversion = 82 %

Tin content = 20.54% (Calc. 21.64%, at 100 % conversion)

Film properties of TBTMA-St-BMA terpolymer

Test	Result
Thickness	100 μm
Hardness (pendulum)	2 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1.5 foot

Table (48)

Preparation of tri-n-butyltin methacrylate-styrene-tri-n-butyltin acrylate terpolymer

TBTMA:St:TBTA = 20:60:20 mole %

Reaction time = 10 hours

Conversion = 75 %

Tin content = 21.70 % (Calc. 22.70%, at 100% conversion)

Film properties of TBTMA-St-TBTA terpolymer

Test	Result
Thickness	90 µm
Hardness (pendulum)	1.8 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1.3 foot

Table (49)

Preparation of tri-n-butyltin methacrylate-styrene-acrylonitrile terpolymer

TBTMA:St:AN = 40:40:20 mole %

Reaction time = 10 hours

Conversion = 90 %

Tin content = 22.38 % (Calc. 23.54 %, at 100 % conversion).

Film properties of TBTMA-St-AN terpolymer

Test	Result
Thickness	100 µm
Hardness (pendulum)	20 seconds
Adhesion	good
Elasticity	good
Cold water resistance	not affected
Hot water resistance	not affected
Alkali resistance:	
5 % NaOH solution	damaged
5 % Na_2CO_3 solution	not affected
Acid resistance:	
5 % H_2SO_4	not affected
Synthetic sea water resistance	not affected
Impact resistance	not affected at 1 foot

From Tables (39-49), it is clear that all films prepared from copolymers and terpolymers involving methyl methacrylate with either tri-n-butyltin acrylate or tri-n-butyltin methacrylate possess good film properties as adhesion, hardness and resistance towards dilute acid and alkaline solutions.

However, organotin copolymers and terpolymers involving styrene (Tables 46-49) showed good adhesion and elastic properties with slight tackiness which may be due to its high organotin moieties (40 mole %).

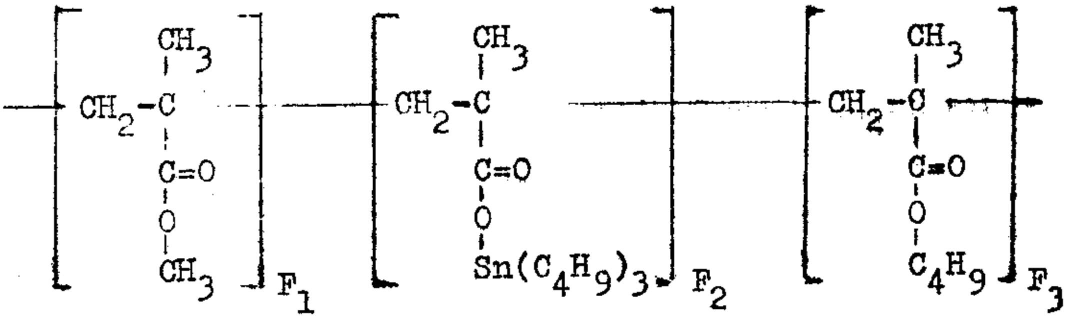
All films showed sensitivity towards dilute sodium hydroxide solution while they were not affected by dilute sodium carbonate solutions. Also the films showed good resistance towards cold water, hot water and synthetic sea water and remained unaffected for prolonged periods of time.

The purpose of this study was to select copolymers and terpolymers suitable for practical, and eventually, industrial applications.

CHAPTER X

Terpolymers with Pendent Organotin Moieties as Antifouling Coatings

Three new organotin polymers with built-in-organotin moieties were prepared from solution polymerization (page 45) of methyl methacrylate, tri-n-butyltin methacrylate and butyl methacrylate, in various molar ratios to produce terpolymers with tin content of 15, 19 and 24 %, which can be represented by the following general structure:



$$-\left[\begin{array}{l} \qquad CH_3 \\ \qquad | \\ CH_2-C \\ \qquad | \\ \qquad C{=}O \\ \qquad | \\ \qquad O \\ \qquad | \\ \qquad CH_3 \end{array}\right]_{F_1}\left[\begin{array}{l} \qquad CH_3 \\ \qquad | \\ CH_2-C \\ \qquad | \\ \qquad C{=}O \\ \qquad | \\ \qquad O \\ \qquad | \\ \qquad Sn(C_4H_9)_3 \end{array}\right]_{F_2}\left[\begin{array}{l} \qquad CH_3 \\ \qquad | \\ CH_2-C \\ \qquad | \\ \qquad C{=}O \\ \qquad | \\ \qquad O \\ \qquad | \\ \qquad C_4H_9 \end{array}\right]_{F_3}-$$

Table (50), illustrates the terpolymer composition, the results of tin analysis and the intrinsic viscosity data for the prepared three terpolymers.

Table (50)

Terpolymer	Terpolymer composition	Tin content		$[\eta_{sp/c}]_{C=0}$
	MMA:TBTMA:BMA	Found	Calc.	
I	0.250 :0.250:0.500	15.97	15.7	0.150
II	0.333 :0.333:0.333	19.14	19.3	0.145
III	0.250 :0.500:0.250	23.95	24.04	0.115

The prepared terpolymers were soluble, colourless ranging from transparent solids to hard rubbery materials and were suitable for film formation. Terpolymer solutions with applicable viscosity were obtained from 50 % solutions in xylene. Unpigmented films were prepared from such terpolymer solutions, on glass and metal plates, and were left to complete drying for several days at room temperature. The films were found to have good elasticity and adhesion properties. Films prepared from terpolymers I and II (Table 50), 15 and 19 % tin content, respectively) were hard enough and tack-free, while films from terpolymer III (24 % tin content) were slightly tacky and did not reach complete dryness even after prolonged periods of time. These results are in agreement with the intrinsic viscosity measurements illustrated in Table (50), which indicate that the terpolymer intrinsic viscosity decreases as the tributyltin moiety in the terpolymer backbone increases. Unpigmented films from such terpolymers, when immersed in slightly alkaline salt solution (pH 8.2), did not develop turbidity or milkiness in the depth of the films, and remained unaffected after 3 weeks of immersion.

Raft Testing:

Test panels were cut to 200x150x3 mm from impact PVC sheets, then the surfaces and edges were roughened by sand-paper. The panels were connected to the testing stand with PVC threads through holes in the panels. After washing and cleaning with methanol, the panels were coated by two successive coats with the unpigmented and pigmented terpolymer formulations. The average film thickness was between 60-90 μ. The testing stand was left at room temperature for one week to ensure complete drying of the films; then submerged in the floating raft launched in the eastern harbour of Alexandria, at a depth of 150 cm from the water surface. Periodic visual and biological examination and photographic recording of the panels were performed. The film conditions like adhesion, cracks, blisters, erosion, ... etc, were also recorded.

Panel immersion in sea water is still an important method for evaluating new antifouling coating devices. In the present work, the prepared organotin polymers (I, II, III, Table 50) were used in seven formulations as unpigmented and pigmented coatings as shown in Table (51) which illustrates the dry film composition of the seven formulations:

Table (51)

Dry Film(x) Composition in Weight percent

Formulation No. / Consituents	Group A		Group B		Group C		
	1	2	3	4	5	6	7
Terpolymer I	100	60	---	---	---	---	---
Terpolymer II	---	---	100	60	---	---	---
Terpolymer III	---	---	---	---	100	60	60
Titanium Dioxide(xx)	---	33	---	40	---	40	33
TPTF	---	7	---	---	---	---	7
Total pigment	---	40	---	40	---	40	40
Total binder	100	60	100	60	100	60	60
Pigment/binder	---	2/3	---	2/3	---	2/3	2/3

(x) Solvent xylene
(xx) Rutile type

It is well known that pigmentation may improve the film properties and may have a role in increasing the permeability of the film, which permits continuous contact between sea water and the toxin centres in the polymer chains leading to simultaneous release of the hydrolyzed toxic groups. Thus, the prepared terpolymers were pigmented essentially with titanium dioxide and in some formulations triphenyltin fluoride (TPTF) was added as an external toxin along with the prepared organotin polymers (Table 51). TPTF is considered to be a strong antifouling agent and less soluble in sea water than tributyltin oxide or fluoride.

In the present investigation, fourteen PVC panels were coated on both sides with the seven formulations (Table 51) in duplicates and were arranged on the testing stand as shown in Fig. (39), i.e. each formulation is represented by four surfaces.

1	2	6	7	6	2	1
3	4	5	7	5	4	3

Fig. (39). Diagram of the testing stand showing the positions of the seven tested formulations.

The advantage of using plastic panels is to eliminate corrosion and rust problems and to avoid the probable problems of incomplete compatibility between the anticorrosive and the top coat. The testing stand was submerged in the sea, in Alexandria eastern harbour; on August 17, 1978. This region is known for its high fertility for most serious fouling organisms all the year round. The physico-chemical and biological conditions near the testing raft were previously reported[68].

Testing Results:

The seven unpigmented and pigmented formulations are classified into three groups, A, B and C; according to the terpolymer composition used in each formulation as illustrated in Table (51). The following results were derived from the periodical inspections throughout 15 months of immersion in sea water:

1. All the fourteen test panels were covered with a heavy slime film. Slime usually occurs to any painted surface submerged in the sea soon after a few days of immersion. It is usually composed of bacteria, diatoms and considerable amounts of organic and inorganic detritus materials. Brown and green algae were the primary foulers detected after 3 weeks of immersion. The rate of algal growth increased rapidly and some panels were covered completely after two months, as shown from Fig. (40b). The rate of slime and algal growth on the panels can be arranged as follows: group $A > B > C$, i.e. the rate is indirectly proportional to the tin content of the organotin polymer. This result agrees with the conclusions previously reported by Ghanem & Abd El-Malek[69], that antifouling compositions prepared

with organotin compounds could not prevent plant fouling.

2. Attachment of animal foulers started by a few number of branacles on some panels during the first month of immersion (Fig. 40a). The attachment began at the edges and spread gradually to the inside of the panels as follows:

a- For group A formulations (1 and 2, Table 51) signs of failure appeared on the fourth month by slight to moderate attachment of some branacles, after heavy accumulation of algae. In the period between the fifth and seventh month, the panels areas were almost completely covered by heavy fouling of branacles, bryozoans and ascidians (Fig. 40d) and only 30 % of the panels areas of group A were left free of fouling. It was observed that the unpigmented terpolymer I (formulation 1) is more efficient than the pigmented one.

b- The antifouling efficiency of group B (formulations (3, 4, Table 51) extended only one month longer than group A. At the end of the 8th month, 40 % of the panels areas of the unpigmented terpolymer II (formulation 3) was still clean, while those of the pigmented ones were completely fouled.

c- Group C formulations (5,6 and 7, Table 51) possessed good antifouling properties against animal fouling for eleven months and all the panels were clean except for a little attack of the edges of the panels (Fig. 40e). After thirteen months, the pigmented formulations 6 and 7 began to fail and about 50 % of the panels areas were heavily fouled. At the end of fifteen months only panels coated with unpigmented terpolymer III (formulation 5) were relatively more successful with about 70 % fouling-free areas, while the pigmented formulations 6 and 7 were almost completely covered with heavy fouling and only small areas were still clean.

3. It seems that all tested organotin polymer formulations possessed better antifouling resistance against tube worms than branacles, which was clearly demonstrated by the early attack of the panels by some branacles which continued through the first six months of immersion, although the ribs of the testing stand (taken as a blank), were heavily fouled with intensive quantities of tube worms reaching 10-12 cm thickness, along with few amounts of branacles as shown in Fig. (40c). The only attack of tube worms on the panels was found at the edges accumulating over an older layer of branacles.

4. All pigmentations showed different degrees of chalking (self polishing) during the inspection period. On passing a finger on the films, some of the pigment with part of the binder was rubbed off. This behaviour was clearly demonstrated for formulations 6 and 7, which may be due to the type of the nature of terpolymer III being softer than terpolymer I and II.

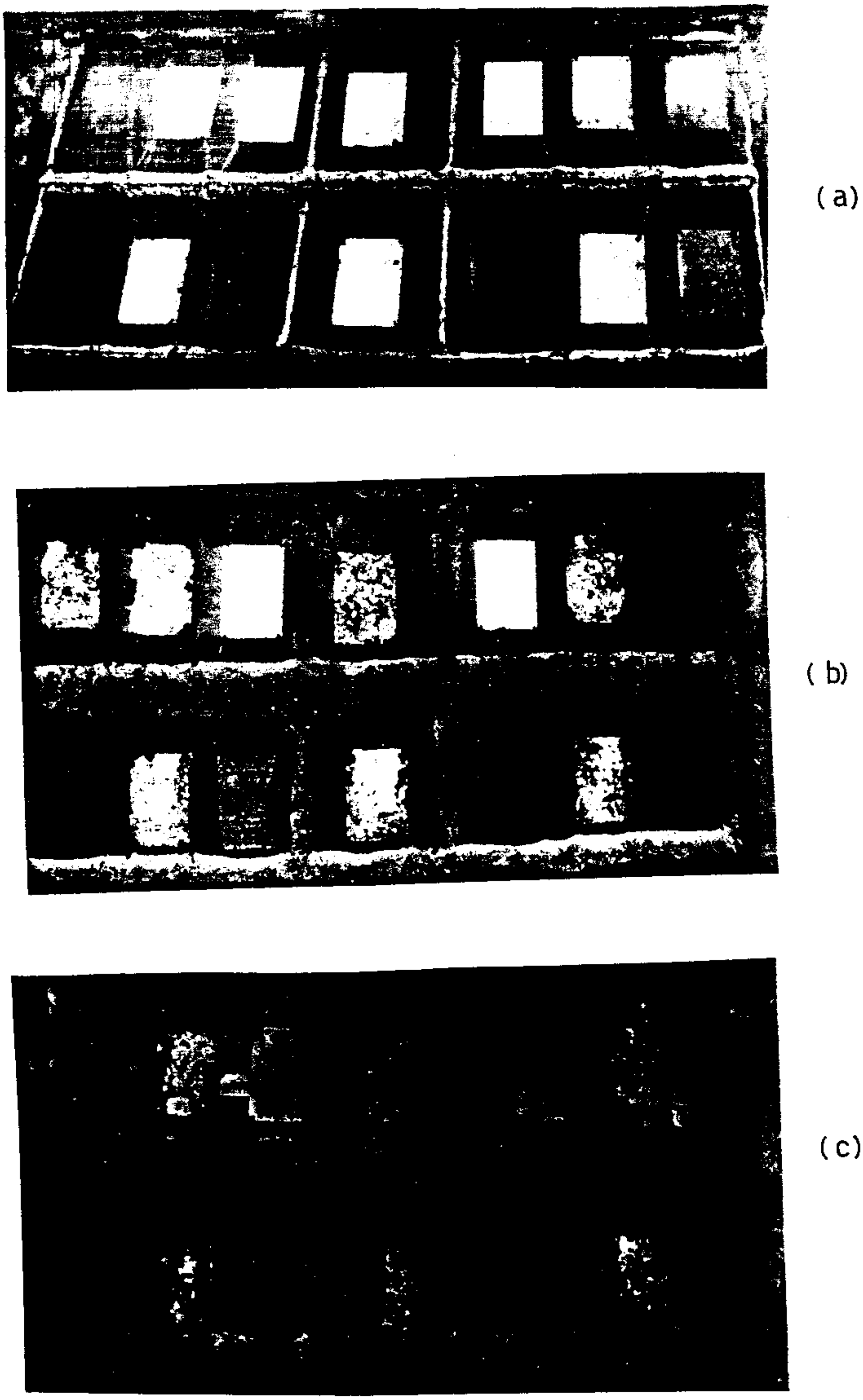


Figure (40). Photographic recording of the testing stand submerged in the eastern harbour of Alexandria for: (a) 21 days, (b) 2 months, (c) 4 months,

REFERENCES

1. W.H. Carothers, J. Amer. Chem. Soc., 51, 2548 (1929).
2. C.A. Barson and J.C. Bevington, J. Polymer Sci., 20, 133 (1956).
3. F.M. Lewis and M.S. Matheson, J. Amer. Chem. Soc., 71, 747 (1949).
4. R.G.R. Bacon, Quart. Revs., 9, 287 (1955).
5. C.V. Schulz and F. Blaschke, Z. Physik. Chem. (Leipzig), B51, 75 (1942).
6. A. Vrancken and G. Smets, Makromol. Chem., 30, 197 (1959).
7. G.F. Santte, R.H. Marchessault, H.G. Clark, J.J. Kearny and V. Stannett, Makromol. Chem., 73, 177 (1964).
8. Y. Bando and Y. Minoura, J. Polymer Sci., A14, 693 (1976).
9. W.A. Pryor and T.R. Fiske, Macromolecules, 2, 62 (1969).
10. T. Alfrey, Jr. and G. Goldfinger, J. Chem. Phys., 12, 205 (1944).
11. F.R. Mayo and F.M. Lewis, J. Amer. Chem. Soc., 66, 1594 (1944).
12. T. Skeist, J. Amer. Chem. Soc., 68, 1781 (1946).
13. B. Vollmert, "Polymer Chemistry", Translated by E.H. Immergut, Springer-Verlag, New York (1973).

14. M. Fineman and S.D. Ross, J. Polymer Sci., 5, 269 (1950).

15. R.M. Joshi and S.L. Kapur, J. Polymer Sci., 14, 508 (1954).

16. P.W. Tidwell and G.A. Mortimer, J. Polymer Sci., part A-1, 3, 369 (1965).

17. A.L. Yezrielev, E.L. Brokhina and Y.S. Roskin, Vysokomol. Soedin, A8, 1670 (1969).

18. T. Kelen and F. Tüdős, J. Macromol. Sci. Chem. 9, 1 (1975).

19. F.R. Mayo and C. Walling, Chem. Rev., 46, 191 (1950).

20. R.D. Burkhart , and N.L. Zutty, J. Polymer Sci., 57, 793 (1962).

21. T. Alfrey, Jr. and G. Goldfinger, J. Chem. Phys., 12, 322 (1944).

22. E.C. Chapin, G.E. Ham and R.G. Fordyce, J. Amer. Chem. Soc., 70, 538 (1948).

23. S.L. Aggarwal and F.A. Long, J. Polymer Sci., 11, 127 (1953).

24. A. Valvassori and G. Sartori, Chem. Eind (Milano), 44, 1091 (1962).

25. G.E. Ham, J. Polymer Sci., A2, 4169 (1964).

26. F.R. Mayo, J. Polymer Sci., A2, 4207 (1964).

27. D.J. Khan and H.H. Horowitz, J. Polymer Sci., 54, 363 (1961).

28. C.J. Evans and P.J. Smith, J. Oil Col. Chem. Assoc., 58, 160 (1975).

29. J.A. Montemarano and E.J. Dyckman, J. Paint Technol., 47, 59 (1975).

30. T.M. Andrews, F.A. Bower, B.R. Laliberte and J.C. Montermoso, J. Amer. Chem. Soc., 80, 4102 (1958).

31. E.F. Jason and E.K. Fields, U.S. Pat. 3,262,915 (1966).

32. G.J.M. Van der Kerk and J.G. Noltes, Ann. N.Y. Acad. Sci., 125, 25 (1965).

33. J. Leebrick, French Pat. 1,400,617 (1965).

34. J.C. Montermoso, T.M. Andrews and L.P. Marinelli, J. J. Polymer Sci., 32, 523 (1958).

35. M.M. Koton, T.M. Kiseleva and R.M. Paribok, Dokl. Akad. Nauk. SSSR, 125, 1263 (1959).

36. N.A. Adrova, M.M. Koton and E.M. Moskvina, Izv. Akad. Nauk. SSSP. Otdel. Khim. Nauk, 1804 (1962).

37. J. Leebrick, U.S. Pat., 3,167,532 (1965).

38. D.A. Kochkin, Z.M. Rzaev, L.A. Sukhareva and P.I. Zubov, Vysokomol. Soedin, A9, 2208 (1967).

39. Z.M. Rzaev and D.K. Kochkin, Dokl. Akad. Nauk, SSSR (English Transl.), Consultants Bureau, Vol. 172, No. 103, January (1967).

40. J. Fujitani, Japan. Kokai 77,139,144 (Cl. Co 9D5/14) (1977); cf. C.A. 88: 106934q (1978).

41. S. Matsuda and H. Kudara, Japan Kokai, 78,30,637 (1978); cf. C.A. 89: 112568k (1978).

42. D. Atherton, V. Verborgt and M.A.M. Winkeler, J. Coatings Technol., 51, 88 (1979).

43. M.M. Koton, J. Polymer Sci., 52, 237 (1961).

44. S.R. Sandler, J. Dannin and K.C. Tson, J. Polymer Sci., A3, 3199 (1965).

45. K.P. Zabotin and L.V. Malysheva, Tr. Khim-Khim. Tekhnol. 1, 47 (1973).

46. R.V. Subramanian, B.K. Grag and J. Corredor, Amer. Chem. Soc., Division of Organic Coatings and Plastics Chemistry, 173rd Meeting 37(1), 77 (1977).

47. P.J. Smith and L. Smith, Chem. in Britain, 11, 208 (1975).

48. H.B. Stoner, J.M. Barnes and J.I. Duff, Brit. J. Pharmacol. 10, 16 (1955).

49. D.E. Gilbert, E.J. Dyckman and J.A. Montemarano, Fluid-Solid Surf. Interact. Proc., Symp. 2nd, 169 (1974).

50. V.J. Castelli and W.L. Yeager, ACS Symp. Ser. 33, Controlled Release Polymeric formulations, Symp. 239 (1976).

51. J. Munch-Petersen, Org. Synth. 41, 62 (1961).

52. R.A. Cummins and P. Dunn, Aust. J. Chem. 17, 185 (1964).

53. H. Gilman and D. Rosenberg, J. Amer. Chem. Soc., 75, 3592 (1953).

54. "Erichsen Catalog for Paint Instruments", p. 15 – 19 and 26 (1959).

55. A. Gardner and G. Sward, "Physical and Chemical Examinations of Paints, Varnishes, Lacquers and Colours", 12th Edition, Gardner Laboratory, INC. Bethesda 14, Maryland, U.S.A., p. 147 (1962).

56. Ibid., p. 450 (1962).

57. "Indian Standard Specifications", IS: 158 (1950).

58. Ibid., 159 (1950).

59. A. Gardner and G. Sward, "Physical and Chemical Examinations of Paints, Varnishes, Lacquers and Colours", 12th Edition, Gardner Laboratory, INC. Bethesda 14, Maryland, U.S.A., p. 160 (1962).

60. P.C. Deb and A.B. Samui, Angew. Makromol. Chem., 80, 137 (1979).

61. M. Izu and K.F. O'driscoll, J. Appl. Polymer Sci., 14, 1515 (1970).

62. S.R. Palit, S.R. Chatterjee and A.R. Mukhurjee, Encyclopedia of Polymer Science and Technology, vol. 3, p. 575, John Wiley & Sons, Inc. (1966).

63. W.M. Ritchey and L.E. Ball, J. Polymer Sci., B4, 557 (1966).

64. J. Muller, Chem. Listy, 48, 1593 (1954); cf. C.A. 49, 5077d (1955).

65. F.M. Lewis, F.R. Mayo and W.F. Hulse, J. Amer. Chem. Soc., 67, 1701 (1945).

66. A.S. Nair and M.S. Muthana, Makromol. Chem., 47, 138 (1961).

67. R.G. Fordyce, J. Amer. Chem. Soc., 69, 1903 (1947).

68. A.F.A. Ghobashy, Proceedings of the 4th International Congress on Marine Fouling and Corrosion, Juan-Les-Pins, France, June 14-18 (1976).

69. N.A. Ghanem and M.M. Abdel Malek, J. Coatings Technol., 51, 29 (1979).

ملخص

فى هذه الرسالة تم تحضير كل من اكريلات ثلاثى بيوتيل القصدير وميثاكريلات ثلاثى بيوتيل القصدير لدراسة البلمرة والبلمرة المشاركه الثنائيه والثلاثيه لهذه المونومرات مع بعض المونومرات الفينيليه الاخرى على الوجه التالى :

١ — تمت دراسة تاثير تركيز المونومر (اكريلات ثلاثى بيوتيل القصدير) وكذلك البادئ للتفاعل على سرعة تفاعل البلمرة لاكريلات ثلاثى بيوتيل القصدير ، وقد وجد ان رتبة التفاعل تساوى واحد ونصف على التوالى :

٢ — بالنسبة لعملية البلمرة المشاركه والثنائيه لاكريلات وميثاكريلات ثلاثى بيوتيل القصدير مع اكريلات الميثيل ، اكريلات الايثيل ، اكريلات البيوتيل ، ميثاكريلات الميثيل ، ميثاكريلات البروبيل ، ميثاكريلات البيوتيل ميثاكريلات الاليل ، الستيرين والاكريلونيتريل ، فقد تم تعيين نسب النشاط التفاعلى لهذه المونومرات بطريقتى فينامين — روس وكيلين — تودوس

وقد اوضحت هذه النتائج (نسب النشاط التفاعلى للمونومرات) ان البوليمر المشارك الناتج من جميع التفاعلات يتكون من وحدات (مونومرات) متكررة بصورة عشوائيه اما البوليمر الناتج من تفاعل ميثاكريلات الاليل مع ميثاكريلات ثلاثى بيوتيل القصدير فيكون على هيئة بوليمر يتكون من وحدات متكرره لنوع واحد من المونومرات يليه الوحدات المتكرره من النوع الاخر فى نفس السلسله .

ايضا اوضحت دراسة البلمرة المشاركه الثنائيه لميثاكريلات ثلاثى بيوتيل القصدير مع كل من ميثاكريلات البروبيل ، ميثاكريلات البيوتيل اكريلات البيوتيل والاكريلونيتريل انه يعطى بوليمر مشارك ازيوتروبى عند النسب الجزيئية الاتيه :

١٩ر٢٣ : ٨٠ر٧٧ ، ٤٣ر٤٨ : ٥٧ر٥١ ، ٥٣ر٧٣ : ٤٧ر٢٦ ،
٤٩ر٩١ : ٥٠ر٠٢ على التوالى . اما بالنسبه للبلمرة المشاركه الثنائيه

لاكريلات ثلاثى بيوتيل القصدير مع المونومرات الفينيليه التى تمت دراستها

فى هذه الرسالة فلم تعطى اى بوليمر مشارك ازيوتروبى على الاطلاق .

٣ ـ اشتملت الرسالة ايضا على دراسة البلمرة المشاركة الثلاثيه للمونومرات العضويه التى تم تحضيرها وكذلك الاكريلونيتريل مع استرات حامض الاكريليك والميثاكريليك وتم بالفعل تعيين تركيب البوليمر الناتج عمليا وقد وجد انه ينطبق مع التركيب المحسوب نظريا باستخدام نسب النشاط التفاعلى للمونومرات التى تم تعيينها فى هذه الدراسة وكذلك الموجودة فى الابحاث المنشوره السابقه .

٤ ـ فى هذه الدراسة ايضا استخدم طيف الاشعة تحت الحمراء لدراسة تركيب المونومرات وكذلك البوليمرات المشاركة الثنائيه والثلاثيه .

٥ ـ تمت دراسة خواص البوليمرات المشاركة الثنائيه والثلاثيه التى تم تحضيرها ووجد انها عديمة اللون شفافة تذوب فى معظم المذيبات العضويه ما عدا الكحول الميثيلى وذات قابلية لتكوين الافلام على السطوح ، ولذلك تم تحضير احدى عشر من البوليمرات المشاركه الثنائيه والثلاثيه وتم اختبار خواص الفيلم المتكون على الاسطح الزجاجيه والمعدنيه لكل بوليمر على حده .

٦ ـ من الفوائد التى تنفرد بها البوليمرات العضويه القصديريه انها تقاوم الحشف البحرى الذى يلتصق بخواطس السفن والمنشآت البحرية ولذلك تم تحضير بوليمر مشارك ثلاثى يحتوى على ميثاكريلات ثلاثى بيوتيل القصدير ، ميثاكريلات الميثيل وميثاكريلات البيوتيل وتمت دراسة مقاومة هذا البوليمر للحشف البحرى دراسة تطبيقية فى ميناء الاسكندريه ولا تزال بعض الالواح المدهونه بهذه البوليمرات تقاوم الحشف البحرى لمدة ١٥ شهرا حتى الان .

تاريخ حياة الطالب

اسم الطالب : عبدالفتاح فاضل شعبان ابوعطيه

تاريخ الميلاد : ١٨/١٢/ ١٩٤٧

جهة الميلاد : ميت يزيد ـ مركز السنطه ـ محافظة الغربيه

المدارس التى تعلمت فيها :

مدرسة ميت يزيد الابتدائيه للبنين

مدرسة القرشيه الاعداديه المشتركه

مدرسة مصطفى صادق الرافعى الثانويه بطنطا

المؤهلات الدراسيه وسنة الحصول عليها :

- بكالوريوس علوم (كيمياء خاصه) يونيو ١٩٧٠ علوم عين شمس
- ماجستير فى الكيمياء يونيو ١٩٧٧ علوم عين شمس

رساله بعنوان

البلمرة والبلمرة المشاركه للمونومرات المحتويه على القصدير

٣

مقدمه إلى
كلية العلوم
جامعة عين شمس

للحصول على درجة
الدكتوراه فى الفلسفه
كيمياء

من

عبد الفتاح فاضل شعبان

ماجستير فى الكيمياء

كلية التربيه
جامعة الزقازيق - فرع بنها

١٩٨٠