

Organotin Polymers. XII. Azeotropy in Binary and Ternary Copolymerization Reactions of Di(tri-*n*-Butyltin) Itaconate with Acrylic Acid Esters, Styrene, and Acrylonitrile

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Synopsis

Binary and ternary copolymerizations of di(tri-*n*-butyltin) itaconate (TBTI) with methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (BA), styrene (ST), and acrylonitrile (AN) were carried out in solution at 70°C in the presence of a free-radical initiator. Experimental terpolymerization data agreed well with calculations based on the Alfrey-Goldfinger equation. The determination of unitary, binary, and ternary azeotropies of the various systems studied was easily handled by a computer. Ternary azeotropic compositions for TBTI-MA-AN and TBTI-EA-AN systems were 37:48:15 and 9:80:11 mol %, respectively. Also, "Pseudo-azeotropic" regions were identified where the deviation between feed and polymer compositions is very small.

INTRODUCTION

Organotin polymers find widespread applications as fungicides, pesticides, wood preservatives, and antifouling coatings.¹⁻⁵ In spite of the great practical interest of organotin polymers, not much work has been done concerning the possibility of preparing a terpolymer with azeotropic composition, i.e., a copolymer whose composition is exactly the same as that of the initial monomer feed. In spite of several attempts, no general solution to the problem of azeotropy in terpolymerization has been given so far.⁶ In our previous works,⁷⁻⁹ we described the kinetics of copolymerization reactions of di(tri-*n*-butyltin) itaconate (TBTI) with various vinyl monomers. It is the aim of the present investigation to synthesize terpolymers with a good compositional homogeneity based on the reaction of di(tri-*n*-butyltin) itaconate with acrylonitrile (AN), styrene (ST), and alkyl acrylates. Also, one of our objectives is the determination of the unitary, binary, and ternary azeotropies for each case.

EXPERIMENTAL

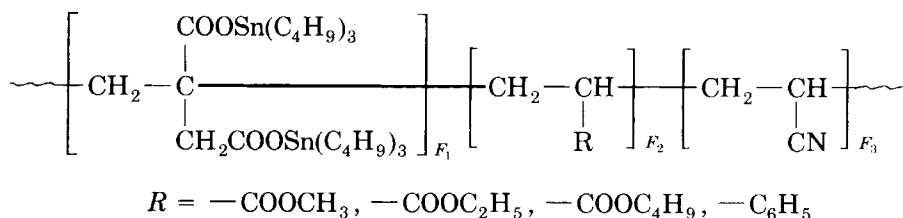
Tri-*n*-butyltin oxide was provided by M & T Chemicals Inc., Rahway, NJ. TBTI was prepared by reaction of itaconic acid with tri-*n*-butyltin oxide according to the method previously described.⁵ Methyl acrylate (MA), ethyl

acrylate (EA), *n*-butyl acrylate (BA), and ST and AN monomers (E. Merck, Darmstadt, products) were purified by distillation under reduced pressure and the middle fractions retained for use.

Binary and ternary copolymer systems were obtained by solution polymerization in toluene (1.5 mol/L) at 70°C, in the presence of 1 mol % azobisisobutyronitrile (AIBN) based on total monomer, according to the method previously described.² Copolymer samples were purified by reprecipitation from methanol, washed, dried, and weighed. Binary and ternary copolymers were analyzed for tin by the method of Gilman and Rosenberg¹⁰; the nitrogen contents of ternary copolymers were determined by a modified Kjeldahl method. The presence of tin and nitrogen in the terpolymer systems facilitates the calculation of the terpolymer compositions.

RESULTS AND DISCUSSION

Four terpolymer systems were prepared by reaction of TBTI with AN and each of MA, EA, BA, or ST. The structure of the prepared terpolymers can be illustrated as follows:



As customarily done, the terpolymer samples were polymerized to low conversions (less than 10%) to allow the use of the terpolymer composition equation. The terpolymer composition of each sample was calculated from tin and nitrogen analyses. The theoretical terpolymer compositions were obtained by the use of Alfrey-Goldfinger terpolymerization equation¹¹ in the form proposed by Khan and Horowitz.¹² The monomer reactivity ratios determined in our previous work,⁷⁻⁹ as well as the literature values¹³ for the binary systems MA-AN, EA-AN, BA-AN, and ST-AN (Table I) were used for calculating the terpolymer composition. The relation between monomer composition in the feed and the composition of the monomer units in the resulting terpolymers is represented in the form of triangular plots. Slocombe¹⁴ proposed the representation of experimental points by means of arrows; the heads of arrows indicate the initial terpolymer composition and the tails the composi-

TABLE I
Monomer Reactivity Ratios for Terpolymerizations of TBTI
with MA, EA, BA, ST, and AN

$M_1-M_2-M_3$	r_{12}	r_{21}	r_{23}	r_{32}	r_{13}	r_{31}
TBTI-MA-AN	0.387	0.671	0.830	0.840	0.441	0.425
TBTI-EA-AN	0.555	0.958	0.950	0.440	0.441	0.425
TBTI-BA-AN	0.521	0.957	0.890	1.200	0.441	0.425
TBTI-ST-AN	0.156	0.645	0.400	0.040	0.441	0.425

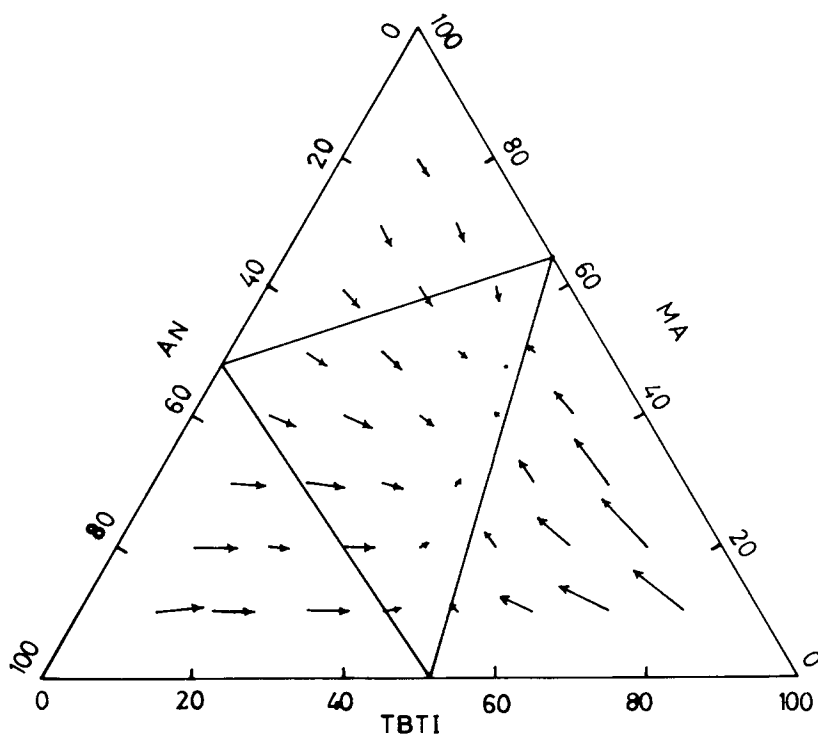


Fig. 1. Instantaneous terpolymer composition as a function of monomer composition for the system TBTI-MA-AN: (—) azeotropic line.

tion of the monomer feed. Terpolymerization of both TBTI-MA-AN and TBTI-EA-AN systems produced compositions represented by arrows pointing toward a well-defined point corresponding to the ternary azeotropic composition. However, compositions produced for TBTI-BA-AN and TBTI-ST-AN systems produced arrows pointing toward a line defined as the azeotropic line,¹⁴ representing the binary azeotropic composition of the monomer pairs. In both cases the arrows were shorter near the ternary azeotropic point or the azeotropic line.

Figures 1 and 2 represent the monomer/terpolymer composition relationship for TBTI-MA-AN and TBTI-ST-AN systems as an example. A computer program written in Fortran IV based on the equation proposed by Khan and Horowitz¹² was used to facilitate the calculations of the ternary monomer-polymer composition relationship and to study the behavior of each monomer during polymerization. All possible compositions were screened and the different azeotropic curves of unitary and binary azeotropies can be graphically plotted.

In the case of unitary azeotropy, the molar amount of one of three monomers is the same in the terpolymer and in the monomer feed. The lines for unitary azeotropy give the composition of a monomer mixture leading to a terpolymer including, for any of the monomers, the same proportion as the monomer feed. The intersection of these unitary azeotropic lines, if any, corresponds to the true or ternary azeotrope and, therefore, indicates the

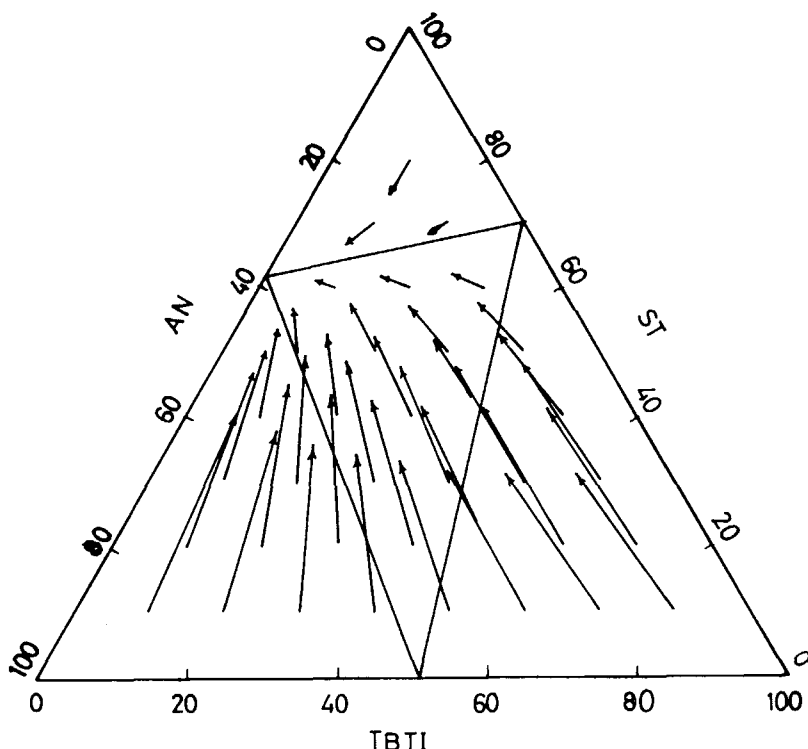


Fig. 2. Instantaneous terpolymer composition as a function of monomer composition for the system TBTI-ST-AN: (—) azeotropic line.

region of lower compositional drift. It is also interesting to determine not only the azeotropic points, but also domains in which the compositional drift is very low. These areas might be termed "pseudo-azeotropic" domains⁶ and are hatched on the diagrams. The unitary azeotropic curves and the difference between the instantaneous terpolymer composition and the monomer feed composition for the four systems studied are illustrated in Figures 3–6. Thus, in the cases of the TBTI-MA-AN and TBTI-EA-AN systems (Figs. 3 and 4) the three curves intersect at one point. These points of intersection correspond to the ternary azeotropic compositions yielding homogeneous terpolymers regardless of conversion.

In the cases of TBTI-BA-AN and TBTI-ST-AN systems (Figs. 5 and 6) the three unitary azeotropic curves do not intersect indicating that there is no ternary azeotropic composition for such systems. The behavior of the TBTI-ST-AN system (Fig. 6) is even more complex, since the line corresponding to the unitary azeotropy for TBTI is actually constituted of two curves. Similar behavior was reported for the unitary azeotropic curve of AN in the acrylonitrile-styrene-4-vinylpyrrolidone system studied by Rios and Guillot.⁶ Also, Wittmer et al.¹⁵ calculated the different unitary azeotropic curves for styrene-methyl methacrylate-methacrylonitrile system and concluded that the unitary azeotropic curve of methyl methacrylate is constituted of two arcs. Our calculations show that pseudo-azeotropic domains may be situated along unitary azeotropic lines or between arcs of these lines

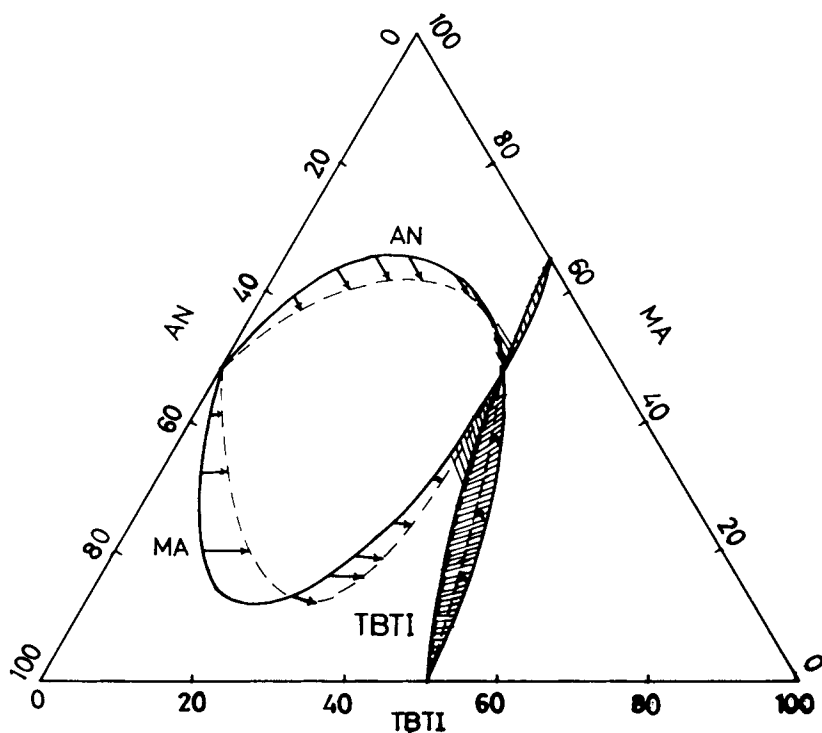


Fig. 3. The unitary azeotropic lines for the system TBTI-MA-AN: (—) monomer composition; (---) terpolymer composition; (hatched area) "pseudo-azeotropic" domains.

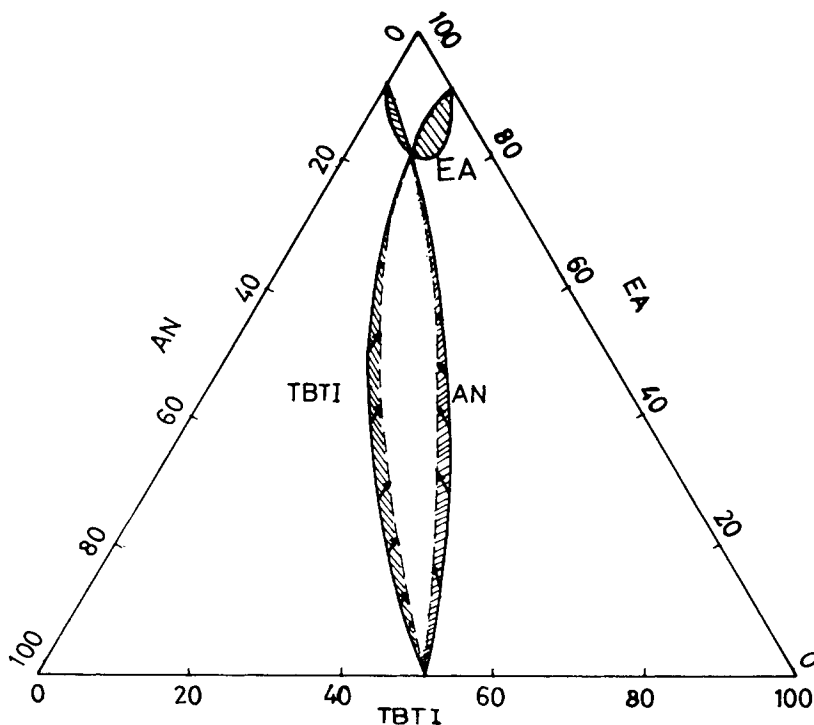


Fig. 4. The unitary azeotropic lines for the system TBTI-EA-AN: (—) monomer composition; (---) terpolymer composition; (hatched area) "pseudo-azeotropic" domains.

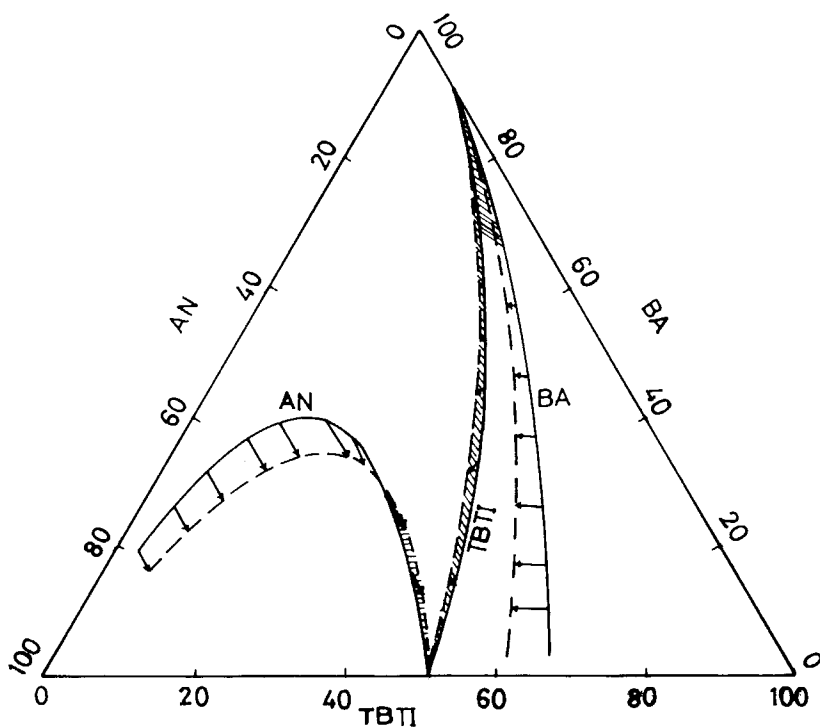


Fig. 5. The unitary azeotropic lines for the system TBTI-BA-AN: (—) monomer composition; (---) terpolymer composition; (hatched area) "pseudo-azeotropic" domains.

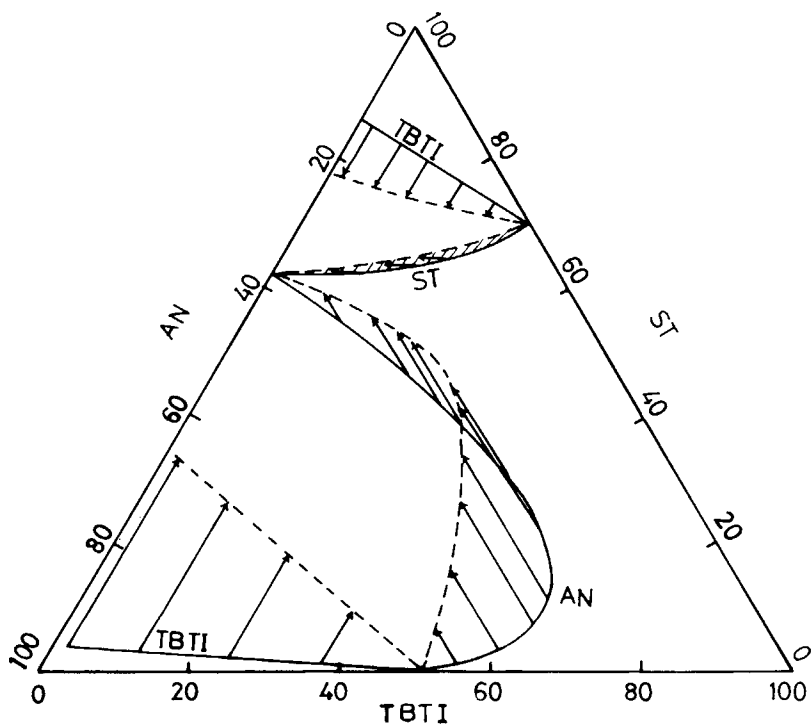


Fig. 6. The unitary azeotropic lines for the system TBTI-ST-AN: (—) monomer composition; (---) terpolymer composition; (hatched area) "pseudo-azeotropic" domains.

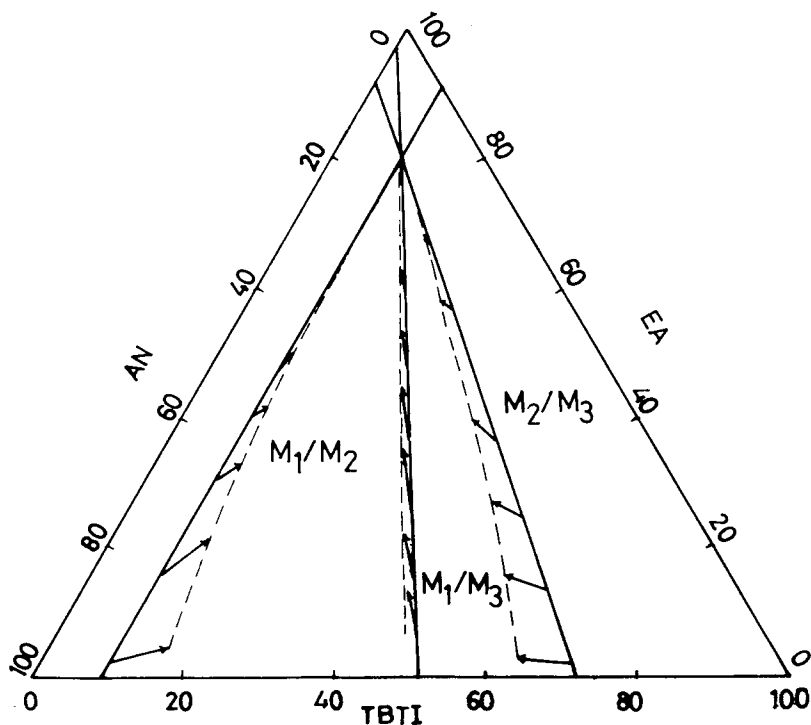


Fig. 7. The binary azeotropic lines for the system TBTI-EA-AN: (—) monomer composition; (---) terpolymer composition.

close enough to one another (Figs. 3 and 4). However, it is not all always valid that the compositional drift remains small along the unitary azeotropic lines as in case of the TBTI-ST-AN system illustrated in Figure 6 which represent very different shapes.

The lines of binary azeotropy, which then correspond to copolymers for which the ratio of two monomers is the same in the terpolymer mixture, also are complex with different shapes and carry the same information relative to true azeotrope and pseudo azeotropic domains. Figures 7 and 8 show the curves of binary azeotropy for TBTI-EA-AN and TBTI-ST-AN systems, respectively. Thus, when a ternary azeotrope does exist, the binary azeotropic curves intersect at the same point (TBTI-EA-AN, Figs. 4 and 7) as expected. Rios and Guillot⁶ reported that whereas, in the case of unitary azeotropy, these curves, one for each monomer always appear, for binary azeotropy, it is possible not to observe the azeotropic line for some monomer pairs. This finding is in agreement with our calculations for the TBTI-BA-AN system (Fig. 9), which shows only two binary azeotropic lines.

From the monomer reactivity ratios given in Table I, it is clear that the individual binary copolymerization reactions of TBTI with each of MA, EA, BA, ST, and AN should have binary azeotropic compositions. Thus, the comonomer compositions correspond to each of binary azeotropy were polymerized to several degrees covering a wide range of conversions. Table II shows the azeotropic feed composition and the copolymer composition as a

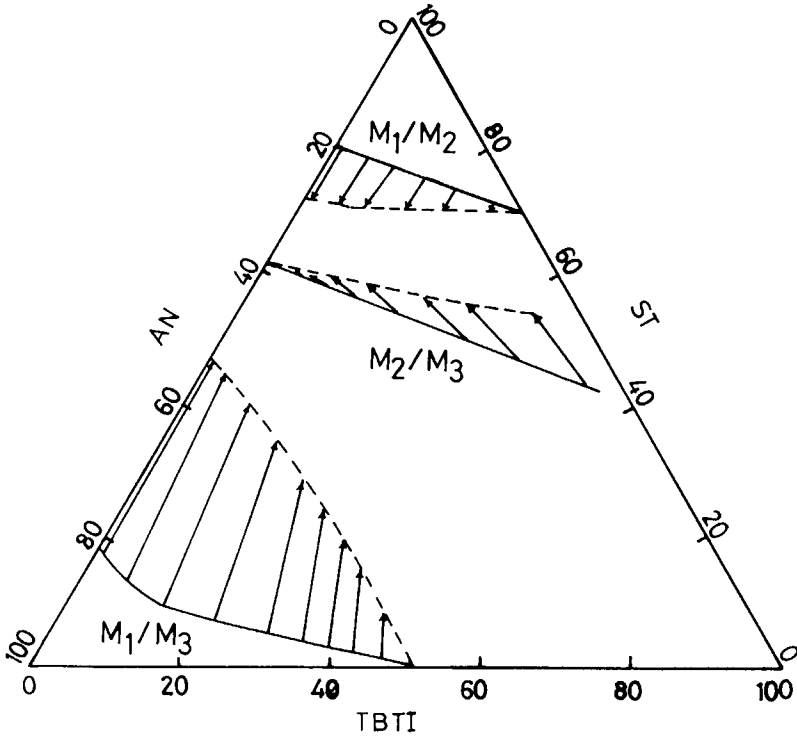


Fig. 8. The binary azeotropic lines for the system TBTI-ST-AN: (—) monomer composition; (---) terpolymer composition.

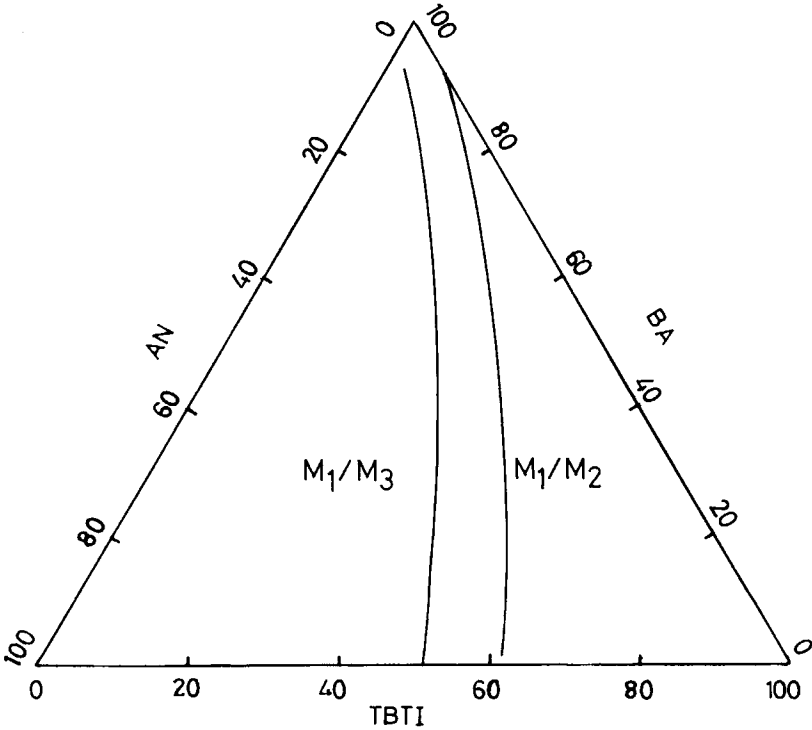


Fig. 9. The binary azeotropic lines for the system TBTI-BA-AN.

TABLE II
Copolymerizations of Individual Binary Azeotropic Compositions
of TBTI with MA, EA, BA, ST, and AN

M_1-M_2	Azeotropic feed compositions (mol %),		Conversion (%)	Sn (%)	Copolymer compositions (mol %),
	M_1	M_2			M_1
TBTI-MA	35.0		17.1	26.8	32.3
			28.4	26.9	32.7
			46.2	27.6	35.8
			72.6	27.2	34.0
TBTI-EA	9.0		14.7	13.6	8.8
			32.3	13.9	9.1
			56.5	13.2	8.4
			87.9	13.3	8.5
TBTI-BA	8.0		13.6	10.5	7.6
			27.2	11.2	8.3
			51.7	10.7	7.8
			77.8	11.1	8.2
TBTI-ST	30.0		11.4	25.1	30.2
			25.7	24.8	29.2
			38.3	25.3	30.9
			67.7	24.9	29.6
TBTI-AN	51.0		12.9	31.4	51.4
			20.1	30.8	45.0
			38.7	31.2	49.1
			58.2	31.3	50.3

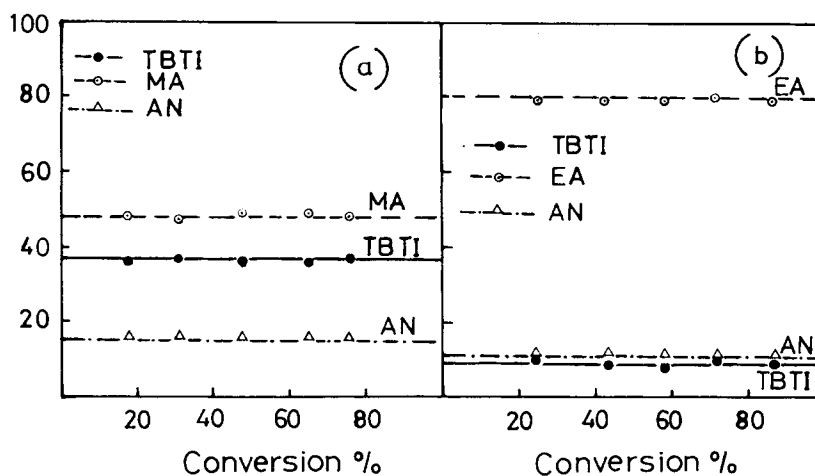


Fig. 10. Variation of average terpolymer composition with conversion for the systems TBTI-MA-AN and TBTI-EA-AN. Lines represent predicted values and (●, ●, and Δ) represent values from nitrogen and tin analyses: (●) TBTI; (Δ) AN; (○) MA (a) or EA (b).

TABLE III
 Terpolymerizations of Selective Unitary Azeotropic Compositions

M ₁ -M ₂ -M ₃	Feed composition (mol %)			Conversion (%)	Sn (%)	N (%)	Unitary azeotrope	Instantaneous terpolymer composition (mol %)					
	M ₁	M ₂	M ₃					Experimental			Calculated		
								M ₁	M ₂	M ₃	M ₁	M ₂	M ₃
TBTT-MA-AN	37.0	49.0	14.0	6.4	28.06	0.59	TBTT	36.14	50.94	12.90	37.0	48.9	14.1
	36.0	31.0	33.0	7.9	28.18	1.47	MA	34.14	35.58	30.28	37.6	31.0	31.4
	16.0	65.0	19.0	8.3	23.49	1.30	AN	20.37	60.47	19.15	19.8	61.2	19.0
TBTT-EA-AN	13.0	63.0	24.0	8.6	17.27	1.90	TBTT	11.70	66.60	21.80	13.0	64.4	22.6
	5.0	84.0	11.0	9.6	10.10	1.20	EA	5.40	83.62	11.00	5.1	84.0	10.9
	26.0	54.0	20.0	4.7	25.12	1.20	AN	26.50	52.00	21.50	24.5	55.5	20.0
TBTT-BA-AN	29.0	59.0	12.0	8.2	23.88	0.62	TBTT	28.50	59.00	12.60	29.0	57.5	13.5
	41.0	46.0	13.0	6.3	27.33	0.60	BA	40.10	44.90	15.00	38.90	46.0	15.1
	6.0	30.0	64.0	7.4	17.17	6.29	AN	10.10	27.30	62.60	10.50	25.5	64.0
TBTT-ST-AN	7.0	82.0	11.0	9.1	11.22	1.73	TBTT	6.30	77.20	16.50	7.0	75.4	17.6
	10.0	62.0	28.0	8.5	14.55	2.99	ST	8.60	61.40	30.00	7.10	62.0	30.9
	21.0	49.0	30.0	6.3	18.39	2.47	AN	12.90	57.70	29.40	13.6	56.4	30.0

TABLE IV
Terpolymerizations of Selective Binary Azeotropic Compositions

M ₁ -M ₂ -M ₃	Feed composition (mol %)			Conversion (%)	Sn (%)	N (%)	Binary azeotrope	Instantaneous terpolymer composition (mol %)					
	M ₁	M ₂	M ₃					Experimental			Calculated		
								M ₁	M ₂	M ₃	M ₁	M ₂	M ₃
TBTI-MA-AN	38.0	41.0	21.0	6.8	28.84	0.87	TBTI/MA	39.1	40.9	20.0	38.2	41.2	20.7
	39.0	42.0	19.0	7.5	28.97	0.83	TBTI/AN	39.9	40.7	19.4	38.7	42.4	18.9
TBTI-EA-AN	9.0	48.0	43.0	8.2	20.52	3.71	MA/AN	13.5	45.2	41.4	13.1	45.8	41.1
	8.0	42.0	50.0	9.1	16.90	4.39	TBTI/EA	9.9	46.3	43.8	9.2	48.0	42.8
	8.0	75.0	17.0	8.6	13.43	1.58	TBTI/AN	7.9	76.2	15.9	8.1	75.5	16.4
	20.0	66.0	14.0	6.3	21.89	0.88	EA/AN	19.6	67.1	13.4	19.0	66.8	14.2
TBTI-BA-AN	20.0	74.0	6.0	5.7	21.06	0.37	TBTI/BA	22.4	71.0	6.7	20.1	73.1	6.8
	16.0	71.0	13.0	7.4	19.86	0.88	TBTI/AN	19.0	66.8	14.3	17.6	68.1	14.3
TBTI-ST-AN	7.0	4.0	89.0	9.6	22.99	8.2	BA/AN	14.1	0.7	85.3	13.3	3.1	83.6
	6.0	77.0	17.0	9.3	8.66	2.72	TBTI/ST	4.3	72.7	23.0	5.4	70.7	23.9
	9.0	12.0	79.0	5.8	13.01	5.99	TBTI/AN	6.4	43.5	50.1	5.6	42.7	51.7

function of conversion and indicates that for each system the copolymer composition remains constant up to high conversions.

The ternary azeotropic compositions for TBTI-MA-AN and TBTI-EA-AN systems (37 : 48 : 15 and 9 : 80 : 11 mol %, respectively) were polymerized to several conversions covering a wide range. The variations of average terpolymer composition as a function of conversion for the two terpolymer systems are illustrated in Figure 10. The results of the average terpolymer compositions, obtained from the analysis of the two terpolymer systems at different conversions, are in good agreement with the predicted values. Also, selective feed compositions corresponding to unitary azeotropy for each system were polymerized to low conversions. The results of the terpolymer composition determined from tin and nitrogen analysis for each case are given in Table III. From Table III it is clear that the experimental terpolymer compositions are in good agreement with those obtained from theoretical calculations. These results indicate the correctness of the six monomer reactivity ratio values given in Table I for each system.

Selective comonomer compositions for each binary azeotropy in terpolymer systems studied were polymerized to low conversion (less than 10%). Table IV show the relationship between the experimental and the theoretical terpolymer composition, and indicates that for each system the experimental values are in good agreement with values obtained from theoretical calculations. From the above results, the free-radical terpolymerization reactions of the systems followed the classical copolymerization theory.

The prepared binary and ternary copolymers were colorless and had rubbery to solid materials soluble in most organic solvents except alcohols. Their infrared spectra showed a strong band at $1630\text{--}1650\text{ cm}^{-1}$ characteristic for the stretching frequency of the carbonyl group due to the carboxylate tin ester. Also, the polymers containing alkyl acrylates showed strong bands at $1725\text{--}1735\text{ cm}^{-1}$ due to the carbonyl group of alkyl esters and showed bands at 2240 cm^{-1} characteristic for the nitrile group.

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