

Organotin Polymers. XV. Azeotropy in Terpolymerization Reactions of Tributyltin Acrylate or Methacrylate with Itaconic Acid or Dimethylitaconate and Acrylonitrile

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SYNOPSIS

Ternary copolymerization of tri-*n*-butyltin acrylate (TBTA) or methylacrylate (TBTMA) with itaconic acid (IA) or dimethyl itaconate (DMI) 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. Ternary azeotropic compositions for TBTA–IA–AN, TBTMA–IA–AN, and TBTMA–DMI–AN systems were 39.0 : 26.1 : 34.9, 51.7 : 10.5 : 37.8, and 00.3 : 66.3 : 33.4 mol %, respectively. Also, “pseudo-azeotropic” regions were identified where the deviation between feed and polymer compositions is very small.

INTRODUCTION

Organotin polymers have long been used as pesticides, as wood preservatives, and in antifouling paint formulations.^{1–3} In our previous work,⁴ the copolymerization parameters of tri-*n*-butyltin acrylate (TBTA) or methacrylate (TBTMA) with acrylic acid esters, styrene, and acrylonitrile have been extensively studied. The addition of a third monomer to the two comonomers in the copolymer can provide additional modification of the physical and mechanical properties for the practical utilization of these polymers. 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. In an earlier article,⁵ we described the binary and ternary copolymerizations of di-(tri-*n*-butyltin) itaconate with acrylic acid esters, styrene, and acrylonitrile (AN). Also, the kinetics of copolymerization reactions of TBTA and TBTMA with itaconic acid (IA) or dimethyl itaconate (DMI) have been investigated.⁶ It is the aim of this investigation to study the kinetics of polymerization of the ternary systems TBTA–

IA–AN, TBTA–DMI–AN, TBTMA–IA–AN, and TBTMA–DMI–AN.

EXPERIMENTAL

Tri-*n*-butyltin oxide was provided by M&T Chemicals Inc., Rahway, NJ. TBTA and TBTMA were prepared according to the method of Cummins and Dunn⁷ by the reaction of bis(tri-*n*-butyltin) oxide with acrylic or methacrylic acids, respectively. Itaconic acid (IA) and dimethyl itaconate (DMI) were obtained from E. Merck, Darmstadt. Azobisisobutyronitrile (AIBN) was crystallized from alcohol, m.p. 102°C.

Ternary copolymer systems were obtained by solution polymerization in DMF (1.5 mol/L) at 70°C in the presence of 1 mol % AIBN according to the method previously described.⁸ The terpolymer samples were polymerized to low conversions (less than 10%) to allow the use of the terpolymer composition equation. The terpolymer samples were purified by reprecipitation from methanol, washed, dried, and weighed. Each sample was analyzed for tin by the method of Gilman and Rosenberg.⁹ The nitrogen content of the terpolymer sample was determined by a modified Kjeldahl method. The terpolymer

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Table I Monomer Reactivity Ratios for Terpolymerization of TBTA or TBTMA with IA, DMI, and AN

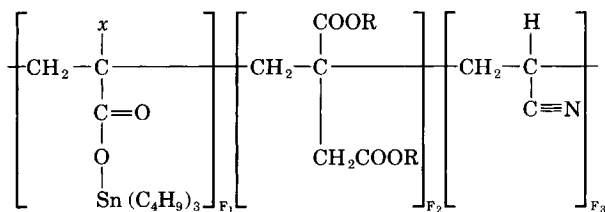
$M_1-M_2-M_3$	r_{12}	r_{21}	r_{23}	r_{32}	r_{13}	r_{31}
TBTA-IA-AN	1.068	0.070	1.750	0.250	0.240	0.997
TBTA-DMI-AN	0.942	0.805	0.630	0.260	0.240	0.997
TBTMA-IA-AN	2.157	0.006	1.750	0.250	0.471	0.474
TBTMA-DMI-AN	1.242	0.869	0.630	0.260	0.471	0.474

The values of r_{12} , r_{21} , r_{13} , and r_{31} are determined in our previous work,^{4,6} whereas the values of r_{23} and r_{32} are from Ref. 12.

composition of each sample was calculated from tin and nitrogen analyses. A computer program written in BASIC based on the Alfrey-Goldfinger terpolymerization equation,¹⁰ in the form proposed by Khan and Horowitz,¹¹ was used to facilitate the ternary monomer-polymer composition calculations. All possible compositions were screened to study the behavior of each monomer during polymerization and to determine each kind of azeotropy (unitary, binary, or ternary) for each system.

RESULTS AND DISCUSSION

The terpolymerization reactions of TBTA-IA-AN, TBTA-DMI-AN, TBTMA-IA-AN, and TBTMA-DMI-AN systems were investigated. The structure of the prepared terpolymers can be illustrated as follows:



where x and $R = \text{H}$ or $-\text{CH}_3$.

The presence of tin and nitrogen facilitate the calculation of the terpolymer composition of each sample. Since the tripolymer equation involves the monomer reactivity ratios of the three separate two-component systems involved, the copolymerization parameters for each binary system determined in our previous work^{4,6} as well as the literature values¹² (Table I) were used to predict the instantaneous terpolymer compositions produced from different feed compositions of each system. 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. Slocombe¹³ proposed the representation of experimental points by means of arrows: The heads of the arrows indicate the initial terpolymer composition, and the tails, the composition of the monomer feed. Terpolymer systems TBTA-IA-AN, TBTMA-IA-AN, and TBTMA-DMI-AN produced compositions represented by arrows pointing toward a well-defined point corresponding to the ternary azeotropic compositions. However, compositions obtained for the TBTA-DMI-AN system did not show any ternary azeotropy. Figure 1 shows the instantaneous terpolymer composition as a function of monomer composition for the TBTA-IA-AN system as an example.

To study the behavior of each monomer during polymerization, a graphic method developed by Rios and Guillot¹⁴ was applied for the determination of azeotropic lines. In case of unitary azeotropy, the

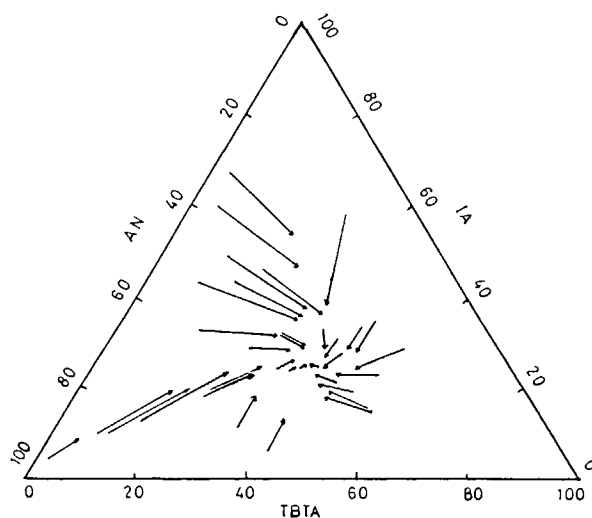


Figure 1 Instantaneous terpolymer composition as a function of monomer composition for the system TBTA-IA-AN.

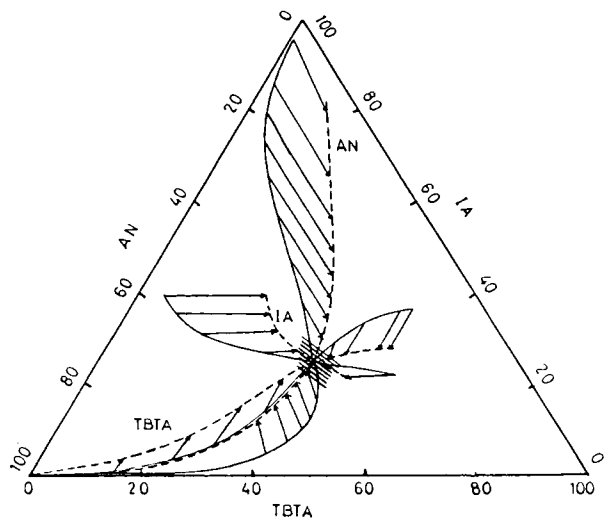


Figure 2 Unitary azeotropic lines for the system TBTA-IA-AN: (—) monomer composition; (----) terpolymer composition; hatched area, "pseudo-azeotropic" domains.

molar amount of one of the three monomers is the same in the terpolymer and in the monomer feed. The intersection of these unitary azeotropic lines, if any, corresponds to the true ternary azeotrope and, therefore, indicates the 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" domains¹⁴

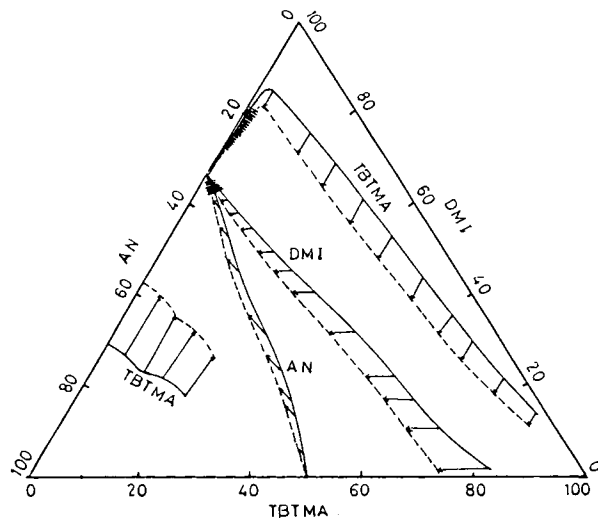


Figure 4 Unitary azeotropic lines for the system TBTMA-DMI-AN: (—) monomer composition; (----) terpolymer composition; hatched area, "pseudo-azeotropic" domains.

and are hatched on the diagrams. The unitary azeotropic curves and the difference between the instantaneous terpolymer composition (dotted lines) and the monomer feed composition (full lines) for the four systems studied are illustrated in Figures 2-5. Thus, in case of TBTA-IA-AN, TBTMA-IA-AN, and TBTMA-DMI-AN systems (Figs. 2-4), the three unitary azeotropic lines intersect at one point. These points of intersection correspond to the ter-

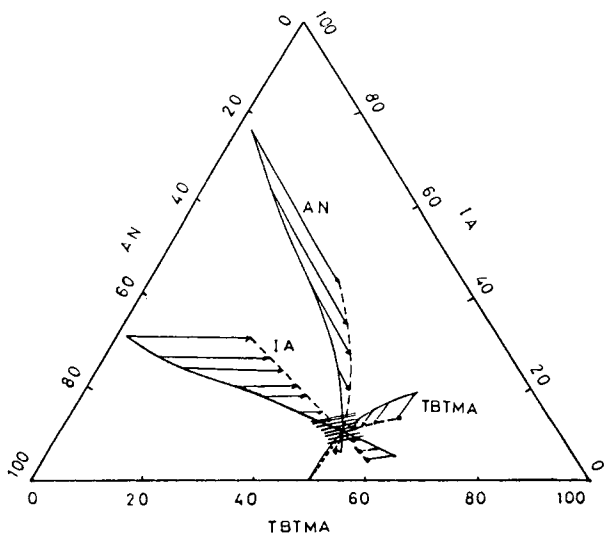


Figure 3 Unitary azeotropic lines for the system TBTMA-IA-AN: (—) monomer composition; (----) terpolymer composition; hatched area, "pseudo-azeotropic" domains.

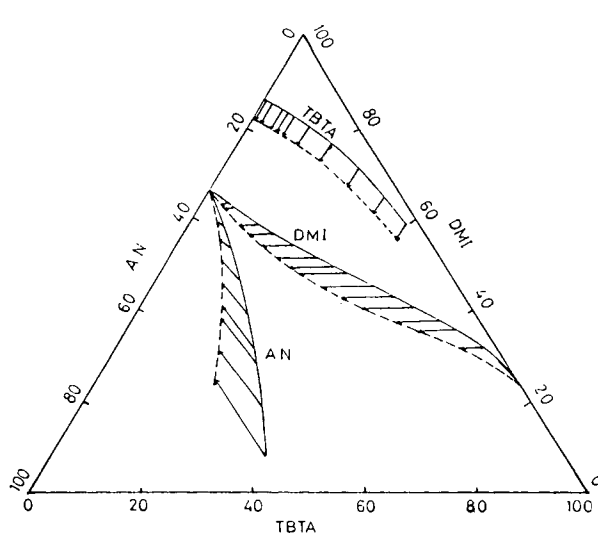


Figure 5 Unitary azeotropic lines for the system TBTA-DMI-AN: (—) monomer composition; (----) terpolymer composition; hatched area, "pseudo-azeotropic" domains.

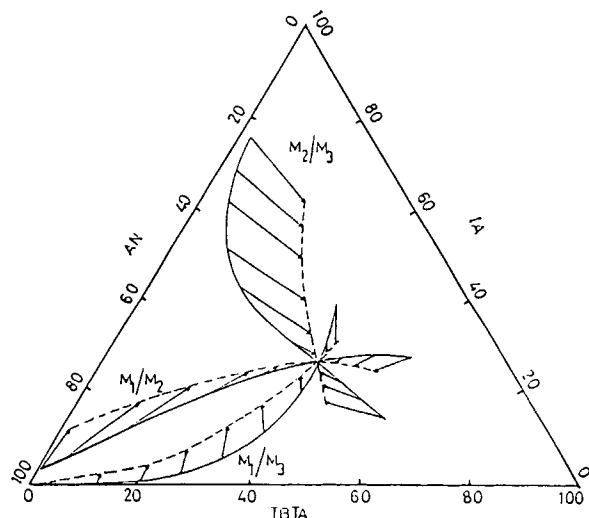


Figure 6 Binary azeotropic lines for the system TBTA-IA-AN: (—) monomer composition; (---) terpolymer composition.

nary azeotropic compositions yielding homogeneous terpolymer regardless of conversion. In case of the TBTA-DMI-AN system (Fig. 5), the three unitary azeotropic lines do not intersect, indicating that there is no ternary azeotropic composition for such a system. The behavior of the TBTMA-DMI-AN system (Fig. 4) is more complex since the lines corresponding to the unitary azeotropy for TBTMA are actually constituted of two curves. Similar behavior was reported for the unitary azeotropic curve of AN in the acrylonitrile-styrene-4-vinyl pyrroli-

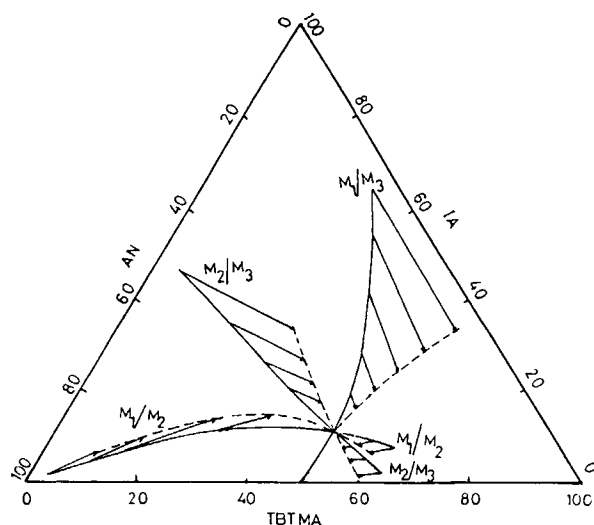


Figure 7 Binary azeotropic lines for the system TBTMA-IA-AN: (—) monomer composition; (---) terpolymer composition.

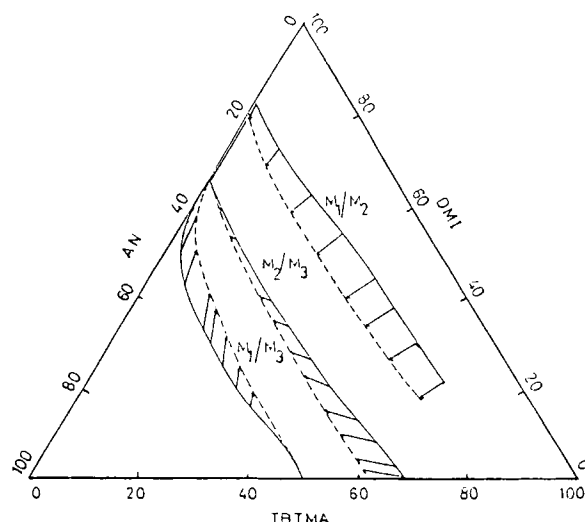


Figure 8 Binary azeotropic lines for the system TBTMA-DMI-AN: (—) monomer composition; (---) terpolymer composition.

done system,¹⁴ the unitary azeotropic curve of methyl methacrylate in the styrene-methyl methacrylate-methacrylonitrile system,¹⁵ and the unitary azeotropic curve of di-(tri-*n*-butyltin) itaconate in the di-(tri-*n*-butyltin) itaconate-styrene-acrylonitrile system.⁵

For the lines of binary azeotropy, which correspond to terpolymers for which the ratios of two monomers is the same in the terpolymer mixture and in the monomer mixture and carry the same information relative to true azeotrope, when a ter-

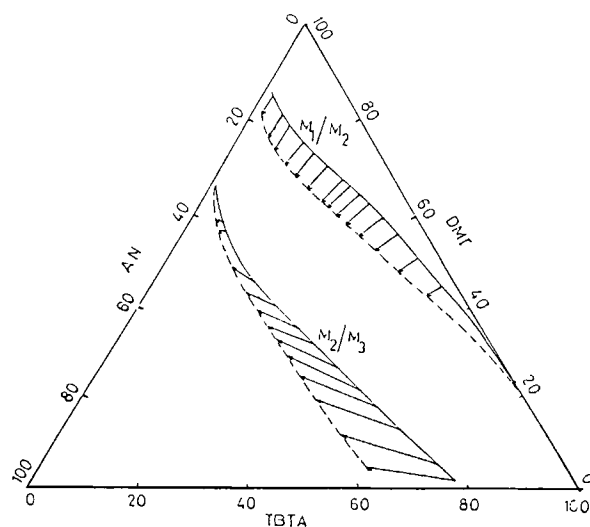


Figure 9 Binary azeotropic lines for the system TBTA-DMI-AN: (—) monomer composition; (---) terpolymer composition.

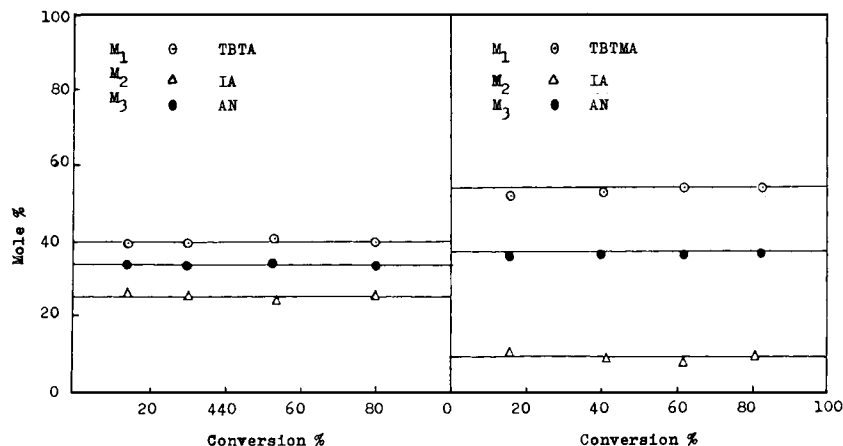


Figure 10 Variation of average terpolymer composition with conversion for the system TBTA-IA-AN and TBTMA-IA-AN; lines represent predicted values and (○, △, ●) represent values from nitrogen and tin analysis.

nary azeotropy exists, the curves intersect at the same point as expected. The binary azeotropic curves and the difference between the instantaneous terpolymer composition (dotted lines) and the monomer feed composition (full lines) for the four systems studied are illustrated in Figures 6-9. Thus, in case of TBTA-IA-AN, TBTMA-IA-AN, and TBTMA-DMI-AN systems (Figs. 6-8), the three binary lines intersect at 39.0 : 26.1 : 34.9, 51.7 : 10.5 : 37.8, and 0.3 : 66.3 : 33.4 mol %, respectively. In case of TBTA-DMI-AN, only two binary azeotropic curves appear for M₁/M₂ and M₂/M₃.

The azeotropic compositions of the terpolymer systems TBTA-IA-AN and TBTMA-IA-AN were polymerized to several degrees covering a wide range of conversions. The variations of average terpolymer compositions as a function of conversion for the two terpolymer systems are illustrated in Figure 10. The results indicate that the terpolymer composition of both systems is constant over a wide range of conversion, which proves that the monomer reactivity ratio values illustrated in Table I are reliable. Selective feed compositions corresponding to unitary azeotropy for each system were polymerized to low

Table II Terpolymerization of Selective Unitary Azeotropic Compositions

M ₁ -M ₂ -M ₃	Feed Composition (mol %)			Conversion (%)	Sn (%)	N (%)	Unitary Azeotropy	Instantaneous Terpolymer Composition (Mol %)					
								Theoretical			Found		
	M ₁	M ₂	M ₃					M ₁	M ₂	M ₃	M ₁	M ₂	M ₃
TBTMA-IA-AN	60.00	18.70	21.30	5.64	27.61	1.41	TBTMA	60.00	13.68	26.32	59.25	15.02	25.72
	32.30	18.30	49.40	7.20	24.16	2.80	IA	41.48	18.30	40.21	40.20	20.19	39.61
	30.20	42.10	27.70	6.92	24.52	1.64	AN	45.66	26.64	27.70	45.76	28.22	26.01
TBTMA-DMI-AN	14.00	75.80	10.10	5.73	10.06	0.97	TBTMA	14.10	71.70	14.20	15.02	72.67	12.31
	20.00	17.20	62.80	6.95	15.98	5.16	TBTMA	20.00	25.78	54.22	19.37	27.47	53.17
	25.70	45.50	28.80	8.64	15.24	2.47	DMI	22.50	45.50	31.95	22.31	46.97	30.72
	27.30	33.20	39.50	7.33	16.75	3.19	AN	23.88	36.62	39.50	23.82	37.62	38.56
TBTA-IA-AN	35.60	17.80	46.60	4.69	23.60	3.16	TBTA	35.60	22.50	41.85	36.03	23.00	41.00
	22.80	29.50	47.70	8.49	21.65	2.80	IA	32.70	29.50	37.80	32.25	32.32	35.43
	25.90	45.50	28.60	5.74	23.02	2.00	AN	37.43	33.97	28.60	37.92	34.06	27.99
TBTA-DMI-AN	6.40	83.10	10.50	6.28	4.69	1.23	TBTA	6.40	78.91	14.69	6.15	80.10	13.75
	25.60	51.50	22.90	4.92	12.99	2.37	DMI	19.55	51.50	28.95	18.03	54.01	27.95
	44.30	43.10	12.60	7.86	19.89	1.40	DMI	35.36	43.10	21.54	34.49	44.83	20.68
	26.40	29.10	44.50	5.76	14.02	4.11	AN	17.72	37.78	44.50	17.41	38.67	43.41

Table III Terpolymerization of Selective Binary Azeotropic Compositions

M_1 - M_2 - M_3	Feed Composition (mol %)			Conversion (%)	Sn (%)	N (%)	Binary Azeotropy	Instantaneous Terpolymer Composition (mol %)					
								Theoretical			Found		
	M_1	M_2	M_3					M_1	M_2	M_3	M_1	M_2	M_3
TBTMA-IA-AN	29.90	10.60	59.70	9.42	24.46	3.45	TBTMA/IA	38.68	13.81	47.51	38.98	14.35	46.70
	42.90	40.40	16.70	5.97	26.41	1.15	TBTMA/AN	54.87	23.77	21.36	55.48	23.97	20.56
	25.90	30.10	44.00	8.46	22.91	2.43	IA/AN	40.39	24.21	35.40	37.81	28.10	34.09
TBTMA-DMI-AN	10.40	73.10	16.50	6.04	6.87	1.64	TBTMA/DMI	9.87	69.40	20.72	9.14	72.30	18.55
	15.00	34.20	50.80	5.21	11.89	4.30	TBTMA/AN	13.43	41.06	45.50	14.28	41.82	43.90
	26.20	39.40	34.40	9.22	16.12	2.85	DMI/AN	22.80	41.20	35.98	23.27	41.75	34.97
TBTA-IA-AN	52.90	27.90	19.20	6.67	25.50	1.69	TBTA/IA	47.65	25.13	27.23	46.59	27.16	26.25
	38.60	14.00	47.40	9.25	24.12	3.35	TBTA/AN	36.02	19.79	44.22	36.82	19.74	43.45
	16.50	43.60	39.90	5.99	21.64	2.49	IA/AN	32.30	35.35	32.34	32.98	34.76	32.25
TBTA-DMI-AN	16.00	73.60	10.40	8.29	10.14	1.19	TBTA/DMI	15.08	69.24	15.67	14.71	70.69	14.60
	20.40	45.80	33.80	7.62	11.67	3.29	DMI/AN	14.62	49.13	36.25	14.79	49.74	35.46
	60.40	13.30	26.30	7.10	24.82	2.60	DMI/AN	41.93	19.50	38.57	42.75	19.27	37.98

conversions. The results of the terpolymer composition determined from tin and nitrogen analysis for each case are illustrated in Table II. From Table II it is clear that the experimental terpolymer compositions are in good agreement with those obtained from theoretical calculations.

Also, selective comonomer compositions for each binary azeotropy in the terpolymer systems studied were polymerized to low conversions (less than 10%). Table III shows the relationship between the experimental and the predicted compositions, which indicate that for each system the experimental values are in good agreement with those obtained from

theoretical calculations. From the above results, the free radical terpolymerization reactions of the systems studied followed the classical copolymerization theory.

The structure of the prepared terpolymers was investigated by IR spectroscopy (as Nujol mull). Figure 11 shows the IR spectra of the TBTA-IA-AN and TBTMA-IA-AN systems. Their infrared spectra showed a strong band at 3000 cm^{-1} due to C-H stretching vibrations, a strong band at 2240 cm^{-1} due to $\text{C}\equiv\text{N}$ of AN, and a band at $1750\text{--}1720\text{ cm}^{-1}$ characteristic for the carboxylate carbonyl group.

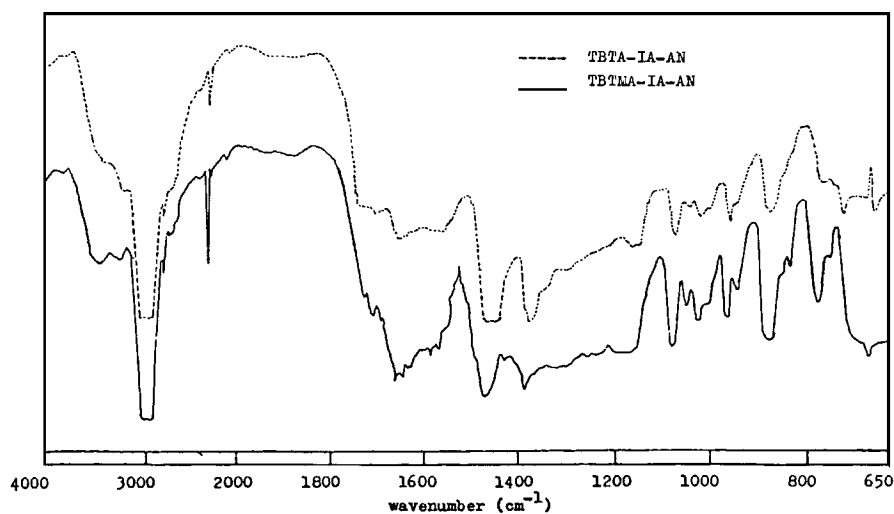


Figure 11 IR spectra of the azeotropic composition of terpolymers: (—) TBTMA-IA-AN; (-----) TBTA-IA-AN.

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