Organotin Polymers. IV. Binary and Ternary Copolymerizations of Tributyltin Acrylate and Methacrylate with Styrene, Allyl Methacrylate, Butyl Methacrylate, Butyl Acrylate, and Acrylonitrile

N. A. GHANEM, N. N. MESSIHA, N. E. IKLADIOUS, and A. F. SHAABAN, *Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt*

Synopsis

The monomer reactivity ratios for the copolymerization of tributyltin acrylate with styrene and allyl methacrylate have been found to be $r_1 = 0.213, r_2 = 1.910$ and $r_1 = 0.195, r_2 = 2.257$, respectively. Also, the copolymerization parameters of tributyltin methacrylate with styrene and allyl methacrylate were as follows: $r_1 = 0.256, r_2 = 1.104$ and $r_1 = 2.306, r_2 = 1.013$. Copolymerization reactions were carried out in solution at 70°C using 1 mole % AIBN, and the copolymer compositions were determined by tin analysis. Ternary copolymerization of the three systems butyl methacrylate–tributyltin methacrylate–acrylonitrile, butyl acrylate–tributyltin methacrylate–acrylonitrile, and styrene–tributyltin acrylate–acrylonitrile have been studied, and the terpolymer composition of each system was determined through tin and nitrogen analyses. The variation of instantaneous and average terpolymer composition with conversion fit satisfactorily the experimental results over a wide range of conversion.

INTRODUCTION

Polymers containing pendent trialkyltin moieties in slowly hydrolyzable form are gaining industrial importance as fungicides and antifouling coatings since their advent in 1958.[1] Careful co- and terpolymerizations allow incorporation of higher proportions of the toxin, its better distribution within the polymer chain, better control of the rate of its release and better control of the polymer physical and storage properties.[2,3] Much of these properties can be achieved through fundamental studies on the copolymerization parameters under specified reaction conditions. Literature data on this relatively novel subject are still little; the copolymerization parameters of tributyltin methacrylate or acrylate with the alkyl esters of methacrylic or acrylic acids as well as acrylonitrile have been obtained.[4–6] In the present work, reactivity ratios were determined for the systems involving tributyltin acrylate and tributyltin methacrylate with both styrene and allyl methacrylate. Six terpolymer compositions, including tributyltin acrylate or methacrylate with styrene, butyl acrylate or butyl methacrylate and acrylonitrile, were polymerized to low conversions to prove the correctness of the determined reactivity ratios. Nitrogen and tin analyses facilitate the calculation of terpolymer composition. The variation of the terpolymer composition at various conversions was also followed.

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EXPERIMENTAL

Tributyltin acrylate (TBTA) and tributyltin methacrylate (TBTMA) were prepared according to the method of Cummins and Dunn[7] by the reaction of tri-n-butyltin oxide with acrylic or methacrylic acids, respectively. Styrene (ST), allyl methacrylate (AMA), butyl acrylate (BA), butyl methacrylate (BMA), and acrylonitrile (AN) monomers (E. Merck, Darmstadt, Germany) were freed from inhibitors by distillation under reduced pressure and the center cuts retained for use. Azobisisobutyronitrile (AIBN) was crystallized from alcohol, mp 102°C.

Copolymers from TBTA and TBTMA with ST and AMA were obtained by solution polymerization in toluene (3 moles/l.) at 70°C in the presence of 1 mole % AIBN according to the method previously described,[5] and the copolymers produced in each case were purified by reprecipitation from 90% methanol, washed, dried, and weighed. Terpolymers including TBTA and TBTMA were similarly prepared. Overall conversion was calculated from the weight of polymer obtained from a known amount of reaction mixture. Tin contents of the copolymers and terpolymers were determined by the method of Gilman and Rosenberg,[8] and the nitrogen contents were determined by a modified Kjeldahl method. The infrared spectra were run on a Beckman 4220 spectrophotometer using the thin film technique.

RESULTS AND DISCUSSION

The copolymerization parameters for TBTA–ST, TBTA–AMA, TBTMA–ST, and TBTMA–AMA systems were determined from the feed composition–copolymer composition relationship, and the conversion was limited to a less than 10% conversion in each case. Table I illustrates the values of the monomer reactivity ratios for the four systems studied calculated by both the Fineman–Ross[9] and Kelen–Tüdös[10] methods, and the standard deviations of the results were calculated by regression analysis. Figure 1 shows the Kelen–Tüdös plots for the four systems studied. The r_1r_2 values (Table I) indicate that the copolymers should have random distribution of the monomer units with a tendency toward alternation, except for the TBTMA–AMA system, which shows a tendency toward the formation of a block copolymer. The copolymerization composition curves are illustrated in Figure 2, which indicate that the systems studied gave no azeotropic copolymers. The prepared copolymers of both TBTA and TBTMA with ST are clear, transparent, and stable even at higher conversions, while the copolymers of AMA with TBTA and TBTMA gave insoluble gel products at higher conversions.

The structure of the prepared copolymers was investigated by IR spectroscopy. Thus, the IR spectra of both copolymers from ST with TBTA and TBTMA were identical and show one carboxyl carbonyl band at 1640 cm^{-1} characteristic for the trialkyltin carboxylates[7] and two strong bands at 750 and 700 cm^{-1} characteristic for monosubstituted aromatic compounds due to ST. Also, the copolymers from AMA with both TBTA and TBTMA were identical and show two carboxyl carbonyl bands at 1730 and 1640 cm^{-1} owing to allyl methacrylate and the alkyltin monomers, respectively. Figure 3 shows the IR spectra of both TBTMA–ST and TBTMA–AMA copolymers.

TABLE I

Monomer Reactivity Ratios for Copolymerizations of Tributyltin Acrylate and Methacrylate with Styrene and Allyl Methacrylate

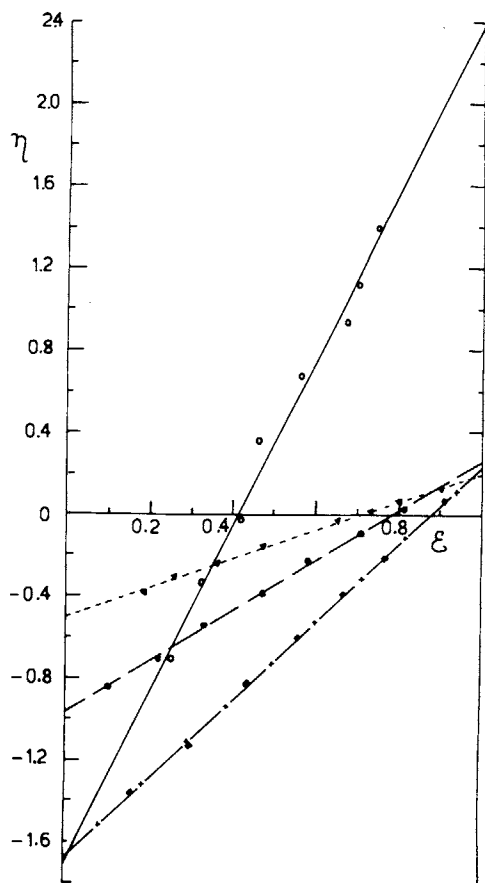| M_1–M_2	Fineman–Ross Method			Kelen–Tüdös Method			
	r_1	r_2	$r_1 r_2$	r_1	r_2	$r_1 r_2$	α
TBTA–ST	0.213 ± 0.010	1.1910 ± 0.049	0.4068	0.219 ± 0.048	1.939 ± 0.038	0.4246	1.1558
TBTA–AMA	0.195 ± 0.005	2.257 ± 0.054	0.4401	0.201 ± 0.009	2.619 ± 0.040	0.5264	5.1901
TBTMA–ST	0.256 ± 0.003	1.104 ± 0.039	0.2826	0.259 ± 0.029	1.108 ± 0.009	0.2869	1.1491
TBTMA–AMA	2.306 ± 0.100	1.013 ± 0.104	2.3359	2.380 ± 0.308	1.057 ± 0.078	2.5156	0.6255

Fig. 1. Kelen–Tüdös plots for copolymerization of (–×–) TBTA–ST, (---) TBTA–AMA, (- -) TBTMA–ST, and (——) TBTMA–AMA: $\epsilon = a^2/(\alpha b + a^2)$ and $\eta = [a(b-1)]/(\alpha b + a^2)$ where $a =$ feed composition, $b =$ copolymer composition, and $\alpha = a_{min} \cdot a_{max}/\sqrt{b_{min} \cdot b_{max}}$.
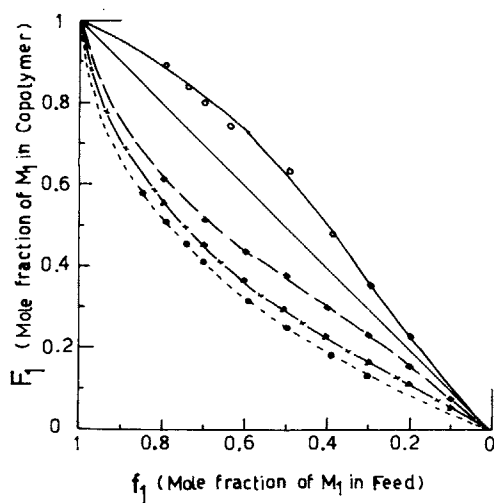

Fig. 2. Dependence of copolymer composition F_1 on comonomer composition f_1 for (–×–) TBTA–ST, (---) TBTA–AMA, (- -) TBTMA–ST, and (——) TBTMA–AMA.
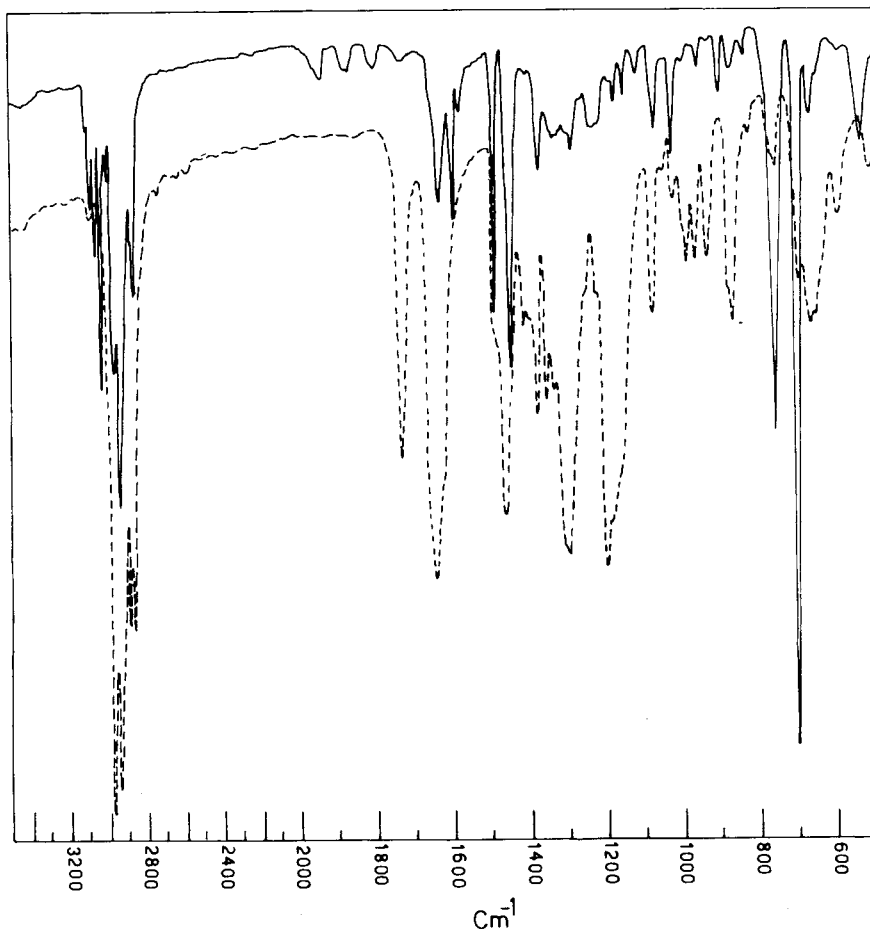
Fig. 3. Infrared spectra for (——) TBTMA–ST and (- - -) TBTMA–AMA.

Terpolymerization Reactions

In our previous work[4-6] the reactivity ratios and azeotropy of binary copolymerizations of TBTMA or TBTA with alkyl methacrylates or acrylates as well as acrylonitrile were studied. It was the aim of the present work to study the terpolymerization of BMA–TBTMA–AN, BA–TBTMA–AN, and ST–TBTA–AN systems. Two feed compositions for each system were selected to investigate the correctness of the reactivity ratios determined by us for organotin mono-

TABLE II
Monomer Reactivity Ratios used in Determining Various Terpolymer Compositions

M_1–M_2–M_3	Monomer reactivity ratios
BMA–TBTMA–AN	$r_{12} = 0.68$, $r_{21} = 0.65^4$; $r_{23} = 0.465$, $r_{32} = 0.467^5$; and $r_{13} = 1.080$, $r_{31} = 0.310^{11}$
BA–TBTMA–AN	$r_{12} = 0.572$, $r_{21} = 0.846^5$; $r_{23} = 0.465$, $r_{32} = 0.467^5$; and $r_{13} = 1.005$, $r_{31} = 1.003^{12}$
ST–TBTA–AN	$r_{12} = 1.910$, $r_{21} = 0.213$; $r_{23} = 0.243$, $r_{32} = 1.008^6$; and $r_{13} = 0.520$, $r_{31} = 0.030^{13}$

TABLE III
Calculated and Found Initial Terpolymer Composition from Tin and Nitrogen Analyses

Charge	Monomers	Feed, mole %	Sn%	N%	Terpolymer Composition, mole %	
					Found	Calculated
	BMA	19.65			26.39	27.80
Ia	TBTMA	20.00	18.71	4.45	24.36	23.24
	AN	60.35			49.23	48.96
	BMA	30.03			34.90	34.81
Ib	TBTMA	30.03	19.69	2.75	29.77	30.88
	AN	39.94			35.32	34.31
	BA	40.02			34.14	32.85
IIa	TBTMA	19.95	19.70	3.16	27.86	27.37
	AN	40.03			37.99	39.78
	BA	19.30			13.27	14.32
IIb	TBTMA	39.17	25.87	2.74	45.64	43.34
	AN	41.53			41.08	42.34
	ST	59.53			66.64	67.06
IIIa	TBTA	20.13	8.26	3.25	7.67	7.10
	AN	20.34			27.68	25.84
	ST	20.42			48.86	47.98
IIIb	TBTA	39.22	12.91	4.60	12.68	11.91
	AN	40.36			38.44	40.11

mers[4-6] and the literature values for BMA–AN,[11] BA–AN,[12] and ST–AN[13] systems. These six terpolymer feeds were polymerized to low conversions (less than 10%), and the terpolymers produced were analyzed for tin and nitrogen. The recovery of nitrogen was found to be about 10% less than the theoretical, which led us to apply a correction factor of 0.5 to all nitrogen results. The initially formed terpolymer composition for each feed was calculated by using the terpolymer composition equation in the form proposed by Khan and Horowitz.[14]
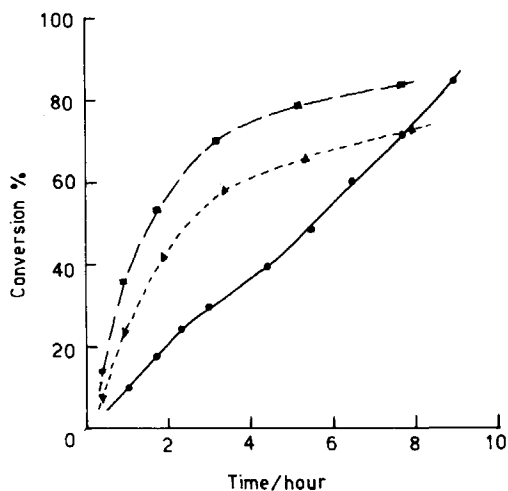

Fig. 4. Overall conversion as a function of time for (- - -) BMA–TBTMA–AN, 19.65:20.00:60.35 mole % feed; (- -) BA–TBTMA–AN, 40.02:19.95:40.03 mole % feed; and (——) ST–TBTA–AN, 59.53:20.13:20.34 mole % feed.
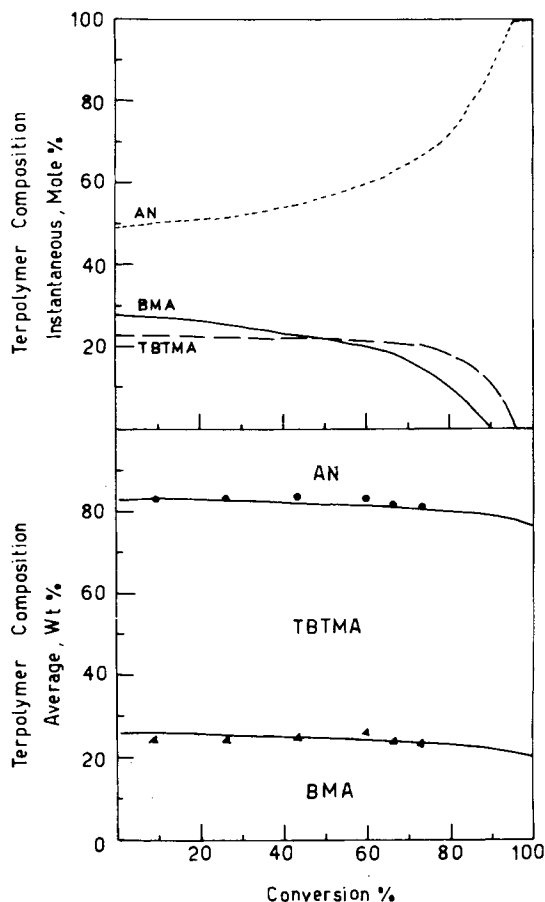
Fig. 5. Variation of instantaneous and average terpolymer composition with conversion for BMA–TBTMA–AN. Lines represent predicted values and (●) and (▲) represent values from nitrogen and tin analyses.

The calculation of the terpolymer composition requires the reactivity ratios of the individual two-component systems. Thus, the reactivity ratios used for calculating the terpolymer composition of each system, determined by us in our previous and present studies as well as the literature values, are illustrated in Table II. The calculated terpolymer compositions are in good agreement with the found results based on nitrogen and tin analyses as shown in Table III, which proves the correctness of the reactivity ratios used for predicting the terpolymer composition.

It is well known that molecular heterogeneity has a direct effect on the physical properties of polymers. Thus, it is aimed to illustrate the changes in terpolymer composition with conversion for the systems BMA–TBTMA–AN, BA–TBTMA–AN, and ST–TBTA–AN (feed charges Ia, IIa, and IIIa, Table III). These feed compositions were polymerized to different levels of conversion, as shown in Figure 4, which illustrates the percent conversion as a function of time for the three systems. The terpolymer composition of each sample was calcu-
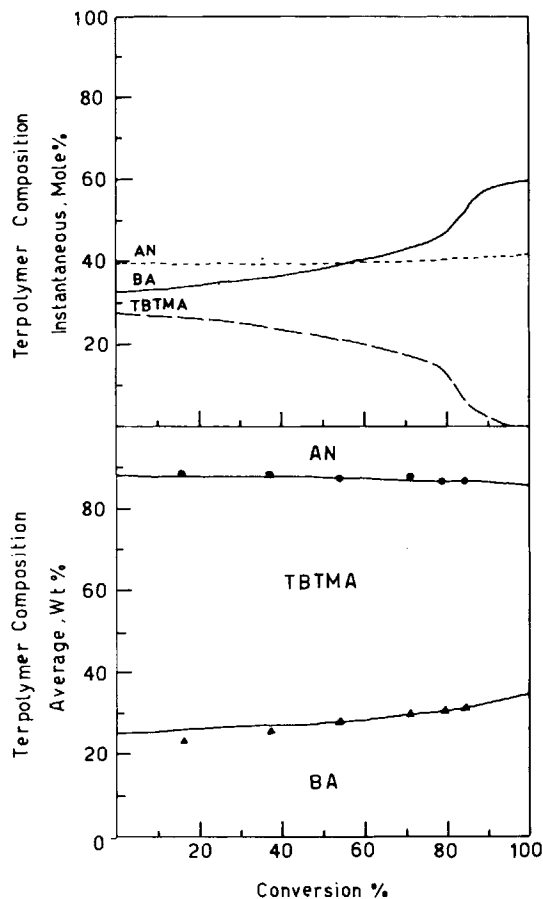
Fig. 6. Variation of instantaneous and average terpolymer composition with conversion for BA–TBTMA–AN. Lines represent predicted values and (●) and (▲) represent values from nitrogen and tin analyses.

lated through nitrogen and tin analyses. A prediction of both the instantaneous terpolymer composition and average terpolymer composition was obtained at each level of conversion for each system by integration of the terpolymer composition equation,[15] assuming that the terpolymer composition is constant within 10% interval. The variation of instantaneous terpolymer composition (mole %) with conversion for the BMA–TBTMA–AN system (Fig. 5) shows that both BMA and TBTMA were completely consumed at 90 and 95% conversions, respectively, followed by AN homopolymer, while for the BA–TBTMA–AN system (Fig. 6) it is clear that TBTMA is completely gone at 95% conversion, after which a copolymer of BA–AN is formed. From the conversion–composition curves for the ST–TBTA–AN system (Fig. 7) it is obvious that both ST and AN disappeared at 93 and 95% conversions, respectively, followed by TBTA homopolymer. The results obtained from the analysis of the three terpolymer systems studied at different levels of conversions, calculated as average terpolymer composition (wt %), are in good agreement with the predicted values as illustrated in Figures 5–7. Also, from these figures it is clear that batch terpolymerization
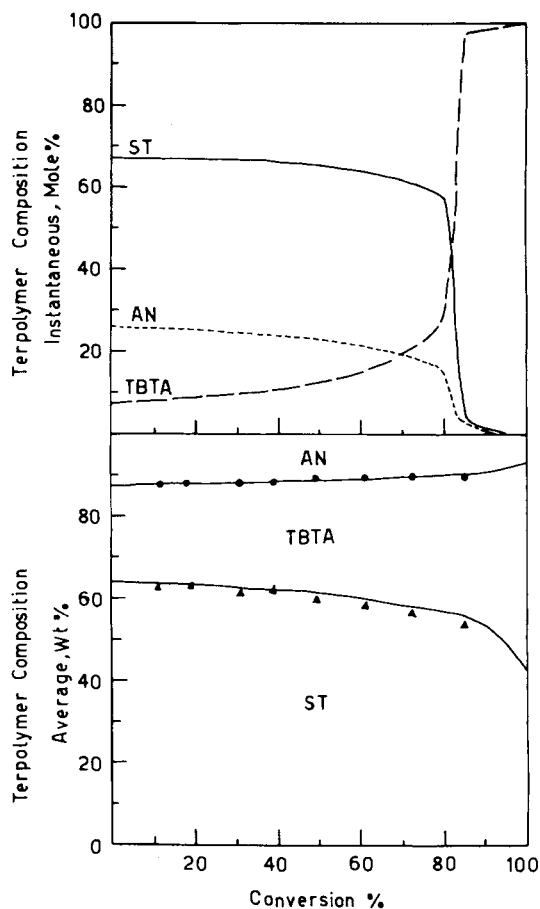
Fig. 7. Variation of instantaneous and average terpolymer composition with conversion for ST–TBTA–AN. Lines represent predicted values and (●) and (▲) represent values from nitrogen and tin analyses.

of the systems studied gives a wide sprectum 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 BMA–TBTMA–AN and BA–TBTMA–AN systems were pale-yellow, rubbery products, while those from the ST–TBTA–AN system were clear, transparent, solid, and suitable for film formation. An extensive program on the industrial applications of copolymers, terpolymers, and polymer blends involving the tributyltin moiety is being carried out.

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