Organotin polymers: 10. Copolymerization parameters for di-(tri-n-butyltin) itaconate with methyl acrylate, ethyl acrylate, *N*-vinyl pyrrolidone and acrylonitrile

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The monomer reactivity ratios for the copolymerization of di-(tri-n-butyltin) itaconate (M_1) with methyl acrylate (M_2), ethyl acrylate (M_2), *N*-vinyl pyrrolidone (M_2) and acrylonitrile (M_2) were found to be $r_1=0.387$, $r_2=0.671$; $r_1=0.555$, $r_2=0.958$; $r_1=0.033$, $r_2=0.185$ and $r_1=0.441$, $r_2=0.425$, respectively. Copolymerization reactions were carried out in solution at 60°C using 1 mol% AIBN, with copolymer compositions being determined by tin analysis. The *Q* and *e* values for di-(tri-n-butyltin) itaconate were calculated from the monomer reactivity ratios determined in the present and previous studies. The sequence distribution of the triad fractions for the systems studied were calculated at azeotropic compositions.

(Keywords: organotin polymers; copolymerization parameters; di(tri-n-butyltin) itaconate; vinyl monomers)

INTRODUCTION

Polymers containing pendent trialkyltin moieties in a slowly hydrolyzable form are gaining industrial importance as fungicides and antifouling coatings since early work in 1958[1]. Careful copolymerization allows incorporation of higher proportions of the toxin, better distribution within the polymer chain and better control of physical and storage properties of the polymer[2,3]. Many of these properties can be achieved through fundamental studies on the copolymerization parameters under specified reaction conditions. Our previous studies have been devoted to binary and ternary copolymerizations of tri-n-butyltin acrylate and methacrylate with various film-forming comonomers[4-8]. Also, the copolymerizations of tri-n-butyltin maleate, and triphenyltin methacrylate with some vinyl monomers were investigated[9-11]. The work has now been extended to study the copolymerization of di-(tri-n-butyltin) itaconate with methyl acrylate, ethyl acrylate, *N*-vinyl pyrrolidone and acrylonitrile.

EXPERIMENTAL

Di-(tri-n-butyltin) itaconate (TBTI) was prepared according to the method of Shaaban *et al.*[12], by the reaction of tri-n-butyltin oxide with itaconic acid. All other monomers used in the copolymerization reactions (methyl acrylate (MA), ethyl acrylate (EA), *N*-vinyl pyrrolidone (NVP) and acrylonitrile (AN)) were obtained from E. Merk, Darmstadt, West Germany and were freed from inhibitors by distillation under reduced pressure and the centre cuts retained for use. Azobisisobutyronitrile (AIBN) was recrystallized from alcohol (m.p. 102°C).

Copolymers from TBTI with MA, EA, NVP and AN were obtained by solution polymerization in toluene ($1.5\,\mathrm{mol\,l^{-1}}$) at 60°C in the presence of 1 mol% AIBN according to the method previously described[5]. The copolymer produced in each case was precipitated from a methanol–water mixture (85%), washed several times, dried and weighed. Overall conversions were kept low and never exceeded 10%. Copolymer compositions were calculated by determining their tin contents through oxidation of the copolymer sample to tin oxide according to the method of Gilman and Rosenberg[13].

RESULTS AND DISCUSSION

In the present investigation the copolymerization parameters for the copolymerization reactions of TBTI with MA, EA, NVP and AN were determined. Typical experimental data for the copolymerization of TBTI with NVP are listed in *Table 1* as an example. Other analytical data of subsequent experiments with various monomers (MA, EA and AN) are not tabulated. The monomer

Table 1 Copolymerization of TBTI with NVP

Feed composition (a)	% Conversion	Sn %	Copolymer composition (b)
1.50	7.35	28.80	0.94
1.19	9.67	28.72	0.92
0.99	8.29	28.57	0.89
0.85	8.77	28.41	0.86
0.66	7.42	28.27	0.83
0.53	7.90	27.52	0.71
0.44	9.11	27.35	0.68

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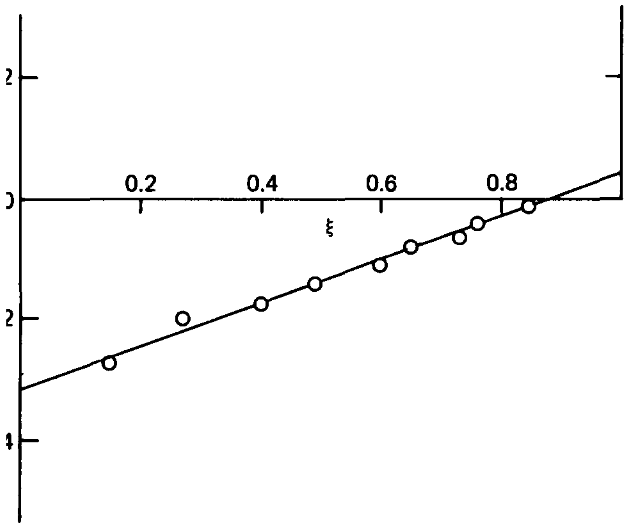
le 2 Monomer reactivity ratios for copolymerization reactions of TBTI with MA, EA, NVP and AN

	Fineman–Ross		Kelen–Tüdös		
	r_1	r_2	r_1	r_2	α
TI-MA	0.42 ± 0.05	0.59 ± 0.03	0.39 ± 0.02	0.67 ± 0.02	0.21
TI-EA	0.42 ± 0.05	0.90 ± 0.03	0.56 ± 0.02	0.96 ± 0.02	0.27
TI-NVP	0.05 ± 0.02	0.20 ± 0.02	0.03 ± 0.01	0.19 ± 0.04	0.82
TI-AN	0.56 ± 0.09	0.47 ± 0.05	0.44 ± 0.05	0.43 ± 0.04	0.29



ıre 1 Kelen–Tüdös plot for copolymerization reaction of TBTI ı MA

$$\xi=\frac{a^2}{\alpha b+a^2} \quad \text{and} \quad \eta=\frac{a(b-1)}{\alpha b+a^2}$$

re a and b are the molar ratios of the comonomer in the feed and olymer, respectively, and

$$\alpha=\frac{a_{\min}a_{\max}}{(b_{\min}b_{\max})^{1/2}}$$

ctivity ratios (r_1 and r_2) for each system were deduced m the analytical data of both the Fineman–Ross[14] and len–Tüdös[15] methods, and the standard deviations of results were calculated by regression analysis as strated in *Table 2*. The monomer reactivity ratios ermined by Fineman–Ross method are in good eement with those obtained from Kelen–Tüdös thod. *Figure 1* shows the Kelen–Tüdös plot for olymerization reaction of TBTI with MA.

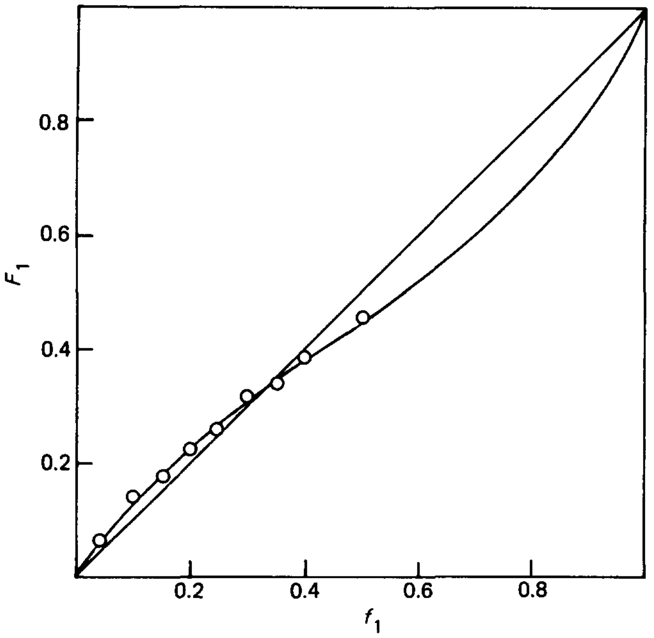


Figure 2 Composition curve for copolymerization reaction of TBTI with MA, curve represents calculated values and (○) represents experimental values, where f_1 = mol fraction of M_1 in feed and F_1 = mol fraction of M_1 in copolymer

Table 3 Triad fractions of M_1 and M_2 in the azeotropic copolymers of TBTI–MA, TBTI–EA, TBTI–NVP and TBTI–AN

M_1–M_2	$f_{111}+f_{222}$	$f_{112}+f_{221}$	$f_{121}+f_{212}$
TBTI–MA	0.22	0.42	0.36
TBTI–EA	0.69	0.20	0.11
TBTI–NVP	0.02	0.22	0.76
TBTI–AN	0.09	0.42	0.50

The copolymer composition curve for the copolyrization reaction of TBTI with MA, calculated on the is of the determined reactivity ratios, is shown in ure 2 along with experimental results. From *Table 2*, it lear that the reactivity ratios (r_1 and r_2) in each system both less than unity, and the copolymerization ctions of these systems should have azeotropic nposition. *Figure 2* shows that the copolymer nposition curve crosses the line representing $f_1 = F_1$ at 5 mol fraction for TBTI–MA. This intersection point resents the azeotropic composition which should yield homogeneous copolymer at various degrees of nversion. The triad fractions of M_1 and M_2 for the otropic composition of the systems studied were culated according to Izu and O'Driscoll[16]. *Table 3* ws that the four azeotropic copolymers have a dom distribution of monomer units in the copolymer chain with a greater tendency toward alternation decreasing in the following order: NVP > AN > MA > EA.

The prepared copolymers were colourless, soluble in most organic solvents and were suitable for film formation.

The Q and e values were calculated from the monomer reactivity ratios using the Alfrey–Price equations[17]:

$$e_1 = e_2 \pm (-\ln r_1 r_2)^{1/2} \tag{1}$$

$$Q_1 = (Q_2/r_2)\exp[-e_2(e_2-e_1)] \tag{2}$$

The Q and e values for TBTI were $Q = 0.589$ and $e = 1.030$ which are in good agreement with the values reported in the literature[18] for the esters of itaconic acid.

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