Organotin polymers: 6. Copolymerization parameters for tri-n-butyltin maleate, acrylate and methacrylate with some vinyl monomers

N. E. Ikladious
Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt

and A. F. Shaaban
Faculty of Science, Chemistry Department, Zagazig University, Benha, Egypt
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The monomer reactivity ratios for the copolymerization of methyl methacrylate (M_1), styrene (M_1), butyl acrylate (M_1) and acrylamide (M_1) with tri-n-butyltin maleate (M_2) have been found to be $r_1 = 15.40$, $r_2 = 0.01$; $r_1 = 6.70$, $r_2 = 0.05$; $r_1 = 9.39$, $r_2 = 0.11$; and $r_1 = 122.44$, $r_2 = 0.06$, respectively. Also, the copolymerization parameters of acrylamide (M_1) with tri-n-butyltin acrylate (M_2) or methacrylate (M_2) were as follows: $r_1 = 0.11$, $r_2 = 0.82$; and $r_1 = 1.46$, $r_2 = 0.85$, respectively. The Q and e values for the organotin monomers (tri-n-butyltin maleate, acrylate and methacrylate) were calculated from the monomer reactivity ratios determined in the present and previous studies. Copolymerization reactions were carried out in solution at 70°C using 1 mol% AIBN, and the copolymer compositions were determined by tin analysis. The structure of the tri-n-butyltin maleate and the prepared copolymers was investigated by i.r. spectroscopy.

Keywords Organotin polymers; copolymerization parameters; tri-n-butyltin maleate; vinyl monomers; acrylamide; Q and e values of organotin monomers

INTRODUCTION

Organotin polymers have very interesting properties especially as binders in antifouling coatings[1]. These polymers were synthesized either by addition polymerization of organotin monomers with appropriate film forming comonomers or by esterification of pendant carboxyl groups on various resins as the reaction between methyl methacrylate–maleic anhydride copolymer with bis-tri-n-butyltin oxide. In previous studies[2-6] the copolymerization parameters of tri-n-butyltin esters of acrylic and methacrylic acids with different vinyl monomers have been illustrated. These values are expected to be very useful in selecting a suitable copolymer for obtaining antifouling coatings with optimum physical properties. The kinetic studies on copolymerization processes have been confined to organotin monomers which could be homopolymerized. It would seem desirable, therefore, to extend the work to a case in which the organotin monomer does not itself polymerize. The aim of the present work is to study the copolymerization reactions of systems involving bis(tri-n-butyltin)maleate with methyl methacrylate, styrene, butyl acrylate and acrylamide. Also, the copolymerizations of tri-n-butyltin acrylate and methacrylate with acrylamide were studied. The reactivity ratio values of the previous and present studies were used to calculate the Q and e values for the tri-n-butyltin monomers used.

EXPERIMENTAL

Bis(tri-n-butyltin)maleate (BTM) was prepared by esterification reaction of maleic anhydride with tri-n-butyltin oxide in benzene at room temperature. The monomer melted at 43°C and its tin content was found to be 33.94% (by the procedure indicated later) against a calculated value of 34.29%. Tributyltin acrylate (BTA) and tributyltin methacrylate (BTMA) were prepared according to the method of Cummins and Dunn[7] by the reaction of tri-n-butyltin oxide with acrylic acid and methacrylic acids, respectively. Methyl methacrylate (MMA), butyl acrylate (BA) and styrene (St) (E. Merck, Darmstadt, Germany) were freed from inhibitors by distillation under reduced pressure and the centre cuts retained for use. Acrylamide (AA) was obtained from Riedel-de Haen AG, Seelze-Hannover. Azobisisobutyronitrile (AIBN) initiator was crystallized from alcohol, m.p. 102°C.

Copolymers from BTM with MMA, St and BA were obtained by solution polymerization in toluene ($3 \text{ mol } l^{-1}$) at 70°C in the presence of 1 mol % AIBN according to the method previously described[3]. Copolymers including AA were similarly prepared using dioxane as a reaction medium. The copolymers produced in each case were precipitated from methanol–water mixture (90%), washed several times, dried and weighed. Overall conversions were kept low and never exceeded 10%. Copolymer compositions were calculated by determining

Table 1 Monomer reactivity ratios for copolymerization reactions of MMA, St, BA and AA with BTM, and AA with BTA and BTMA

M₁–M₂	Fineman–Ross		Kelen–Tüdös		Yezrielev *et al.*		
	r_1	r_2	r_1	r_2	α	r_1	r_2
MMA–BTM	15.40 ± 0.98	0.01 ± 0.02	14.57 ± 2.03	−0.01 ± 0.02	0.0171	14.63 ± 0.91	−0.01 ± 0.02
St–BTM	6.70 ± 0.39	0.05 ± 0.10	6.67 ± 0.99	0.05 ± 0.06	0.0937	6.79 ± 0.54	0.07 ± 0.05
BA–BTM	9.39 ± 0.21	0.11 ± 0.08	8.91 ± 0.79	0.02 ± 0.07	0.1649	9.03 ± 0.66	0.02 ± 0.09
AA–BTM	122.44 ± 6.04	0.06 ± 0.20	111.78 ± 14.70	−0.11 ± 0.07	0.0084	114.88 ± 6.20	−0.11 ± 0.06
AA–BTA	0.11 ± 0.02	0.82 ± 0.06	0.11 ± 0.01	0.82 ± 0.01	0.3034	0.11 ± 0.01	0.82 ± 0.01
AA–BTMA	1.460 ± 0.40	0.85 ± 0.10	1.56 ± 0.34	0.89 ± 0.14	0.3600	1.55 ± 0.32	0.88 ± 0.11

their tin contents through oxidation of the sample to tin oxide according to the method of Gilman and Rosenberg[8]. The infra-red spectra were run on a Beckman 4220 spectrophotometer using the thin film technique.

RESULTS AND DISCUSSION

In the present investigation the copolymerization parameters for MMA, St and BA with BTM were determined. Also, the copolymerization of AA with BTM, BTA or BTMA were studied. The copolymerization parameters r_1 and r_2 for the systems studied were deduced from the analytical data by Fineman–Ross[9], Yezrielev *et al.*[10] (YBR) and Kelen–Tüdös[11] methods, and the standard deviations of the results were calculated by regression analysis as illustrated in *Table 1*. *Figures 1–3* show the
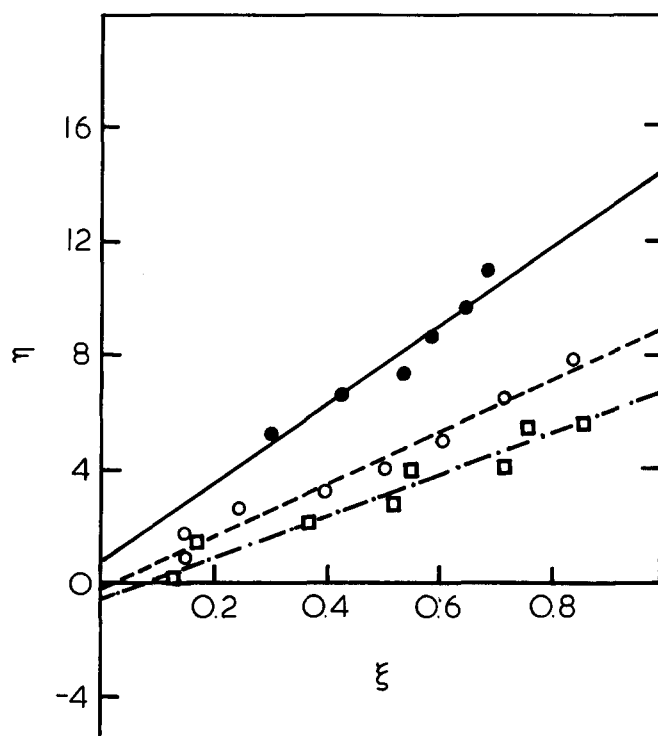
Kelen–Tüdös plots for the six systems. It is clear from *Table 1* that there is good agreement between the values of the reactivity ratios calculated by the three methods. The negative values obtained for r_2 in both MMA–BTM and AA–BTM systems may be due to differences in the graphical methods used and to the experimental error in tin analysis.

Because the solubility characteristics of acrylamide are very different from those of tributyltin acrylate and methacrylate, it was difficult to locate a suitable reaction medium. Best results were obtained with dioxane, which gave a homogeneous reaction solution for values between 0.5 and 0.9 mole fraction of the organotin monomer in the initial monomer concentration.

The composition curves of the six binary copolymerization reactions studied are illustrated in *Figure 4*. *Table 1* shows that in the case of the four copolymerization reactions involving tributyltin maleate with either MMA, St, BA or AA, the monomer reactivity ratio values of the maleate monomer (r_2) are nearly equal to zero, which indicates that the organotin maleate ester is incapable of undergoing homopolymerization. It is clear from *Figure 4* that the copolymers of MMA–BTM, St–BTM, BA–BTM and AA–BTM systems show a much higher content of F_1 than does the monomer mixture. The monomer reactivity ratio values of the vinyl monomers copolymerized with BTM are much greater than unity, especially in the case of AA, which shows that the monomer sequence in these four copolymers consists of larger blocks of the comonomer units interrupted by single molecules of BTM. The $r_1 r_2$
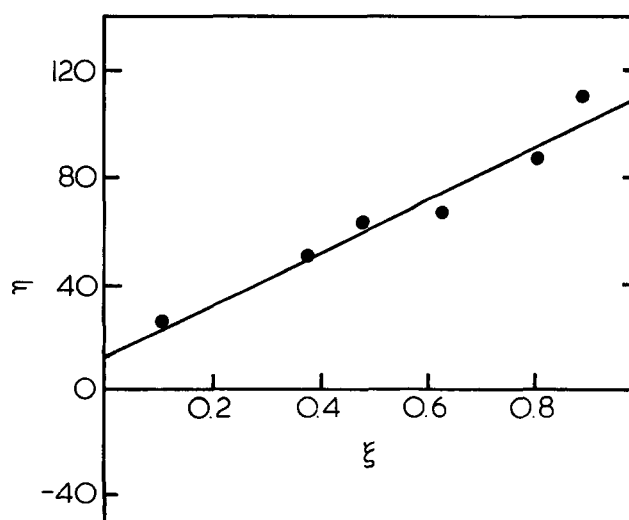
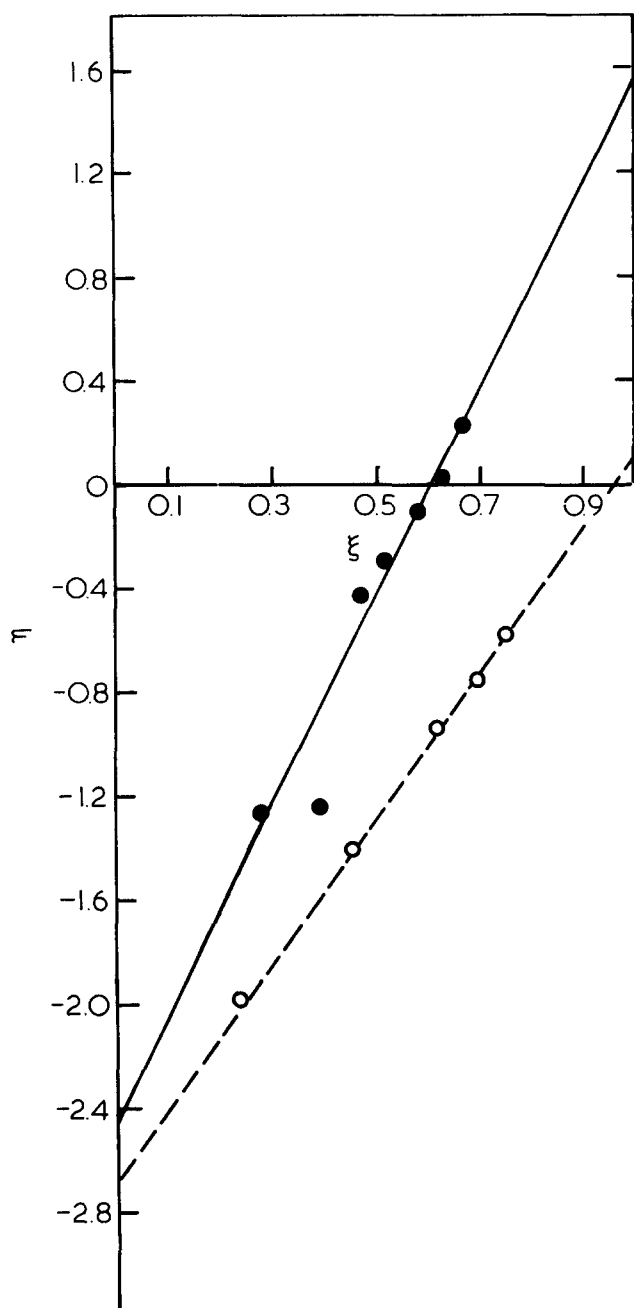**Figure 1** Kelen–Tüdös plots for copolymerization reactions of MMA–BTM (————), BA–BTM (– – –) and St–BTM (–·–·–):

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

where a = feed composition, b = copolymer composition and

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

Figure 2 Kelen–Tüdös plot for copolymerization reaction of AA–BTM

Figure 3 Kelen–Tüdös plots for copolymerization reactions of
AA–BTA (———) and AA–BTMA(– – –)

Figure 4 Composition curves for copolymerization reactions of
(a) MMA–BTM, (b) St–BTM, (c) BA–BTM, (d) AA–BTM,
(e) AA–BTA and (f) AA–BTMA systems

value for AA–BTA system (0.091) indicates that the copolymer should have a random distribution of the monomer units with a tendency towards alternation, while for the AA–BTMA system the r_1r_2 value (1.24) illustrates a low tendency of the monomers to alternate and the copolymer should be composed mainly of small sequences of monomeric units of the same type. *Figure 4* indicates that all systems studied gave no azeotropic copolymers except for the AA–BTA system, whose composition curve crosses the line at $F_1=f_1=0.17$ mole fraction.

The prepared copolymers were colourless, soluble in organic solvents and film forming except that of AA–BTM copolymer which was a powdery solid product.

The structure of the prepared copolymers was investigated by i.r. spectroscopy. *Figure 5* shows the i.r. spectra of BTM monomers and its copolymer with BA.
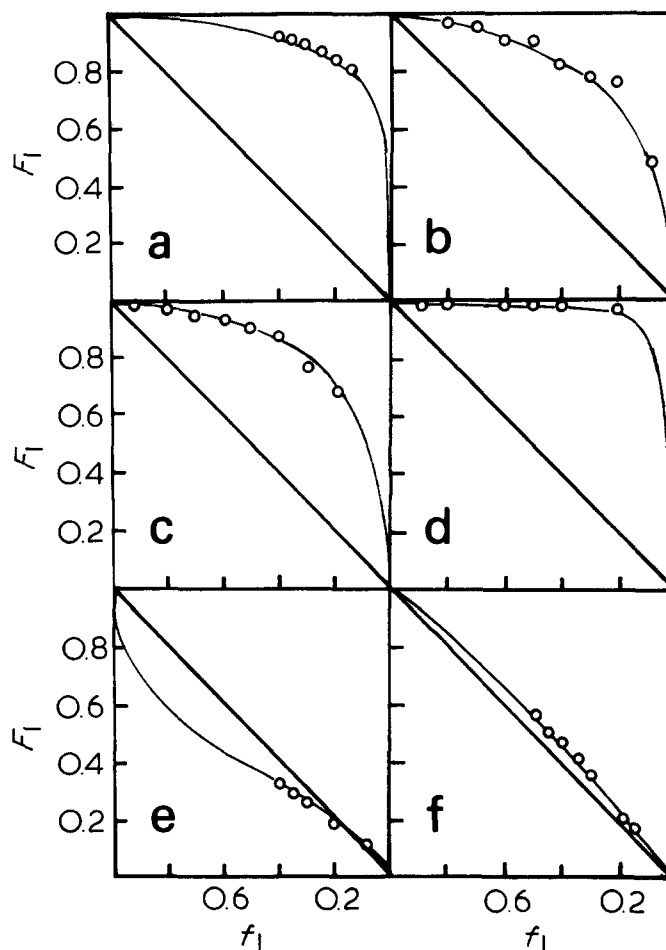
The more characteristic peaks of these spectra are those corresponding to the carboxylate group of the tetraco- and pentaco-oriented tin atom at 1640 and 1565 cm^{-1}, respectively. The spectrum shows another peak at 1725 cm^{-1} characteristic of the carbonyl group due to BA. Also the copolymers from AA with both BTA and BTMA were identical and show two bands, one characteristic of the carboxylate group of tin at 1650 cm^{-1} and the other at 3350 cm^{-1} due to the NH band of AA.

The Q and e values were calculated from the monomer reactivity ratios by using the Alfrey–Price equations[12]:

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

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

The Q and e values which represent the extent of resonance stabilization and the polarity of the double bond, respectively, in a monomer and its radical are extensively tabulated by Young[13] from earlier copolymerization data. Thus, the average Q and e values for BTM, BTA and BTMA were obtained by using the monomer reactivity ratios of the present and previous work[2-6] and the Q and e values[13] for the vinyl monomers. The average Q and e values for BTM, BTA and BTMA were calculated and are summarized in *Table 2*, and have been found to be
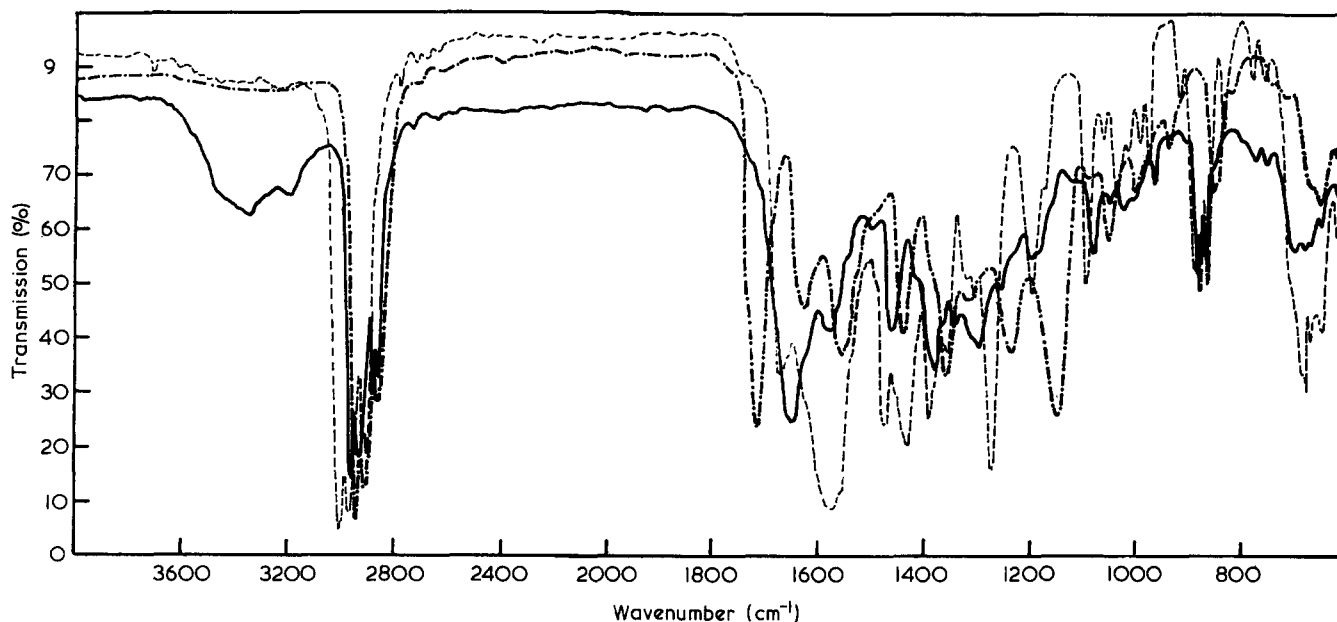
Figure 5 Infra-red spectra for BTM monomer (– – –), BA–BTM copolymer (– · – · –) and AA–BTA copolymer (———)

Table 2 Calculated Q and e values for BTM, BTA and BTMA

Monomer	Q	e
BTM	0.05	1.40
BTA	0.38	0.74
BTMA	0.62	0.57

comparable with the Q and e values reported in the literature[13] for the esters of maleic, acrylic and methacrylic acids, respectively.

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