

Organotin Polymers. VII. Copolymerization of Triphenyltin Methacrylate with Some Acrylic and Methacrylic Acid Esters

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Synopsis

The monomer reactivity ratios for the copolymerization of triphenyltin methacrylate with methyl acrylate, ethyl acrylate, and butyl acrylate have been found to be $r_1 = 2.58$, $r_2 = 0.66$, $r_1 = 2.37$, $r_2 = 0.43$, and $r_1 = 1.27$, $r_2 = 0.39$, respectively. Also, the copolymerization parameters of triphenyltin methacrylate with methyl methacrylate and butyl methacrylate were as follows: $r_1 = 0.94$, $r_2 = 0.99$, and $r_1 = 0.68$, $r_2 = 0.83$, respectively. Copolymerization reactions were carried out in solution at 70°C using 1 mol % AIBN, and the copolymer compositions were determined by tin analysis. The sequence distribution of the alternating diad fractions for the systems studied were calculated at various feed compositions. The structure of the triphenyltin methacrylate monomer as well as its azeotropic copolymer with butyl methacrylate were investigated by IR spectroscopy.

INTRODUCTION

The triorganotin compounds show a high activity against fungi¹ and have been widely used commercially with no adverse effects on those applying them. A further application of the triorganotins, particularly the tributyl- and the triphenyl-tin derivatives, is in the field of marine antifouling paints.^{2,3} The active life time of antifouling paints may be extended considerably if the organotin compounds is incorporated into a polymer network.⁴ The controlled release of the organotin toxicant from the organotin polymer matrix into the water makes the antifouling coating an extremely effective one. Careful co- and terpolymerizations allow incorporation of higher proportions of the toxin, its better distribution within the polymer chain, and better control of the polymer physical and storage properties.^{5,6} Much of these properties can be achieved through fundamental studies on the copolymerization parameters under specified reaction conditions. Reactivity ratio values for the copolymerization reactions of organotin monomers are very scarce in the literature. Our previous studies⁷⁻¹² were confined to the determination of the monomer reactivity ratios for tributyltin acrylate, methacrylate, and maleate with different film forming comonomers. The work is now extended to study copolymerizations of triphenyltin methacrylate with acrylic and methacrylic acid esters.

EXPERIMENTAL

Triphenyltin hydroxide was provided by M & T Chemicals, Inc., Rahway, N.J. Triphenyltin methacrylate (PTMA) was prepared according to Koton,¹³ where

TABLE I
Monomer Reactivity Ratios for Copolymerizations of PTMA with MA, EA, BA, MMA, and BMA

M_1-M_2	Fineman-Ross method			Kelen-Tüdös method		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
PTMA-MA	2.48 ± 0.15	0.63 ± 0.06	1.56	2.58 ± 0.13	0.66 ± 0.03	1.70
PTMA-EA	2.31 ± 0.12	0.42 ± 0.04	0.97	2.37 ± 0.16	0.43 ± 0.04	1.02
PTMA-BA	1.17 ± 0.09	0.35 ± 0.07	0.41	1.27 ± 0.14	0.39 ± 0.05	0.50
PTMA-MMA	1.08 ± 0.03	1.09 ± 0.09	1.18	0.94 ± 0.05	0.99 ± 0.05	0.93
PTMA-BMA	0.64 ± 0.01	0.78 ± 0.04	0.50	0.68 ± 0.03	0.83 ± 0.04	0.56
						α
						0.22
						0.17
						0.28
						0.92
						1.21

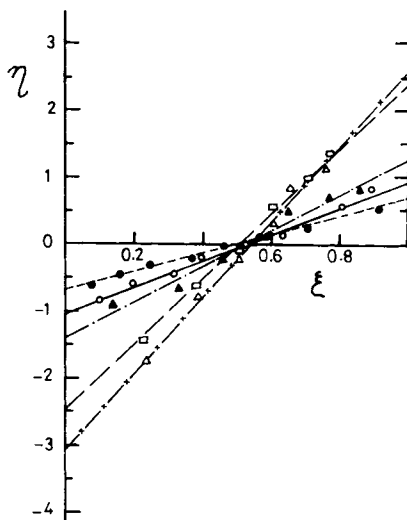


Fig. 1. (— + —) PTMA-MA; (---) PTMA-EA; (-·-·-) PTMA-BA; (—) PTMA-MMA; (· · · · ·) PTMA-BMA: $\xi = a^2/(\alpha b + a^2)$ and $\eta = a(b - 1)/(\alpha b + a^2)$, where a = feed composition, b = copolymer composition, and $\alpha = a_{\min} \times a_{\max}/\sqrt{b_{\min} \times b_{\max}}$.

methacrylic acid was esterified by triphenyltin hydroxide, and the product was recrystallized from light petroleum, mp 85–87°C. Methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (BA), and methyl methacrylate (MMA) were obtained from E. Merck (Darmstadt, Germany) and were purified by vacuum distillation before use. *n*-Butyl methacrylate (BMA) was prepared from methacrylic acid according to the method of Munch–Petersen.¹⁴ Azobisisobutyronitrile (AIBN) initiator was crystallized from alcohol, mp 102°C.

The copolymers were obtained by solution polymerization in toluene (3 mol/L) at 70°C with 1 mol % AIBN according to the method previously described.⁸ Overall conversions were limited to less than 10% in every case. In all cases, the obtained copolymers were soluble in the reaction medium, and were recovered by precipitation in methanol. They were dissolved again, reprecipitated, washed, dried, and weighed. Tin contents of the monomer and copolymers were determined by the method of Gilman and Rosenberg.¹⁵ The infrared spectra of the tin-containing monomer and its copolymers were run on a Beckman 4220 Spectrophotometer.

RESULTS AND DISCUSSION

The copolymer composition was calculated from tin analysis. The copolymerization parameters for PTMA with MA, EA, BA, MMA, and BMA were determined from the feed composition–copolymer composition relationship according to the Fineman–Ross¹⁶ and Kelen–Tüdös¹⁷ methods. Table I illustrates the monomer reactivity ratios r_1 and r_2 for the five systems, and the standard deviations of the results calculated by regression analysis. Figure 1 shows the Kelen–Tüdös plots for the five systems studied.

The copolymer composition curves for the studied systems were calculated

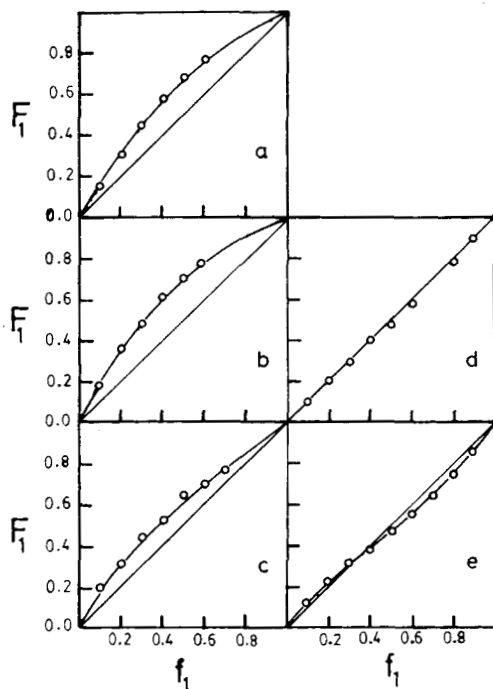


Fig. 2. Composition curves for copolymerization reactions of (a) PTMA-MA, (b) PTMA-EA, (c) PTMA-BA, (d) PTMA-MMA, and (e) PTMA-BMA.

on the basis of the determined reactivity ratio values and are shown in Figure 2 along with the experimental results. It is clear from the results obtained (Table I and Figure 2) that the copolymerization reactions of PTMA with the studied acrylic acid esters (MA, EA, and BA) gave no azeotropic copolymers. Since the reactivity ratio values of PTMA (r_1) in these systems are higher than 1, the resulting copolymers should contain blocks of PTMA. However, the copolymerization reaction of PTMA with MMA show an ideal behavior since the r_1 and

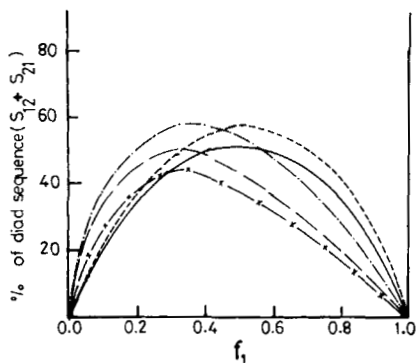


Fig. 3. Dependence of % diad sequence ($S_{12} + S_{21}$) on comonomer composition f_1 for (—x—) PTMA-MA, (---) PTMA-EA, (···) PTMA-BA, (—) PTMA-MMA, and (- - - -) PTMA-BMA.

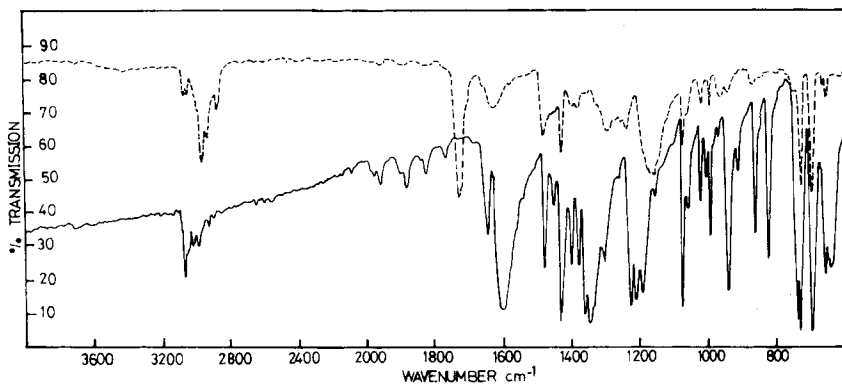


Fig. 4. Infrared spectra for (—) PTMA monomer and (-----) PTMA-BMA azeotropic copolymer.

r_2 values are almost equal to 1 (Table I) which is also clear from its copolymer composition curve (Fig. 2). The monomer reactivity ratio values for PTMA-BMA system are both less than unity (Table I), indicating that the copolymer would be expected to contain a significant amount of alternating monomer unit sequences along the polymer chain, and the copolymerization reaction of this system should have an azeotropic composition. Figure 2 shows the the copolymer composition curve crosses the line representing $f_1 = F_1$ at 0.34 mole fraction. This intersection point represents the azeotropic composition which yields a homogenous copolymer at various degrees of conversion.

The sequence distribution of the comonomers in the systems studied were calculated from the obtained reactivity ratio values according to Izu and O'Driscoll.¹⁸ The variation in the sequence distribution of the alternating diad fractions (S_{12} and S_{21}) with feed composition are represented in Figure 3. It is clear from Figure 3 that copolymers from PTMA with acrylic and methacrylic acid esters have maximum alternation at $f_1 = 0.35$ and $f_1 = 0.5$ mole fraction, respectively. Also, Figure 3 shows that the tendency towards alternation increases with increasing the length of the alkyl chain in the acrylic and methacrylic acid esters (e.g., BA > EA > MA). These findings are in agreement with our previous work^{8,9} on the copolymerization of tributyltin methacrylate with acrylic and methacrylic acid esters and with the work of Zaboltn and Malysheva¹⁹ on copolymerization of tributyltin acrylate with alkyl acrylates. Eginbaev et al.²⁰ reported that the dominant influence on the reactivity of alkyl acrylates or methacrylates was steric and not electronic, and the steric hindrance in the copolymerization increased with increasing the length of the alkyl chain.

The prepared copolymers of PTMA with acrylic and methacrylic acid esters are solid and clear products soluble in most organic solvents and suitable for film formation. These triphenyltin copolymers are found to form an insoluble gel product when heated above 80°C.

Figure 4 illustrates the infrared spectra of PTMA monomer and its copolymer with BMA. Thus, the IR spectrum of PTMA monomer has an absorption band at 1640 cm^{-1} corresponding to ν C=O of the triphenyltin carboxylate group, while the spectrum of the azeotropic PTMA-BMA system shows the same band at 1625 cm^{-1} as well as a band at 1725 cm^{-1} due to the ν C=O of BMA.

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