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Copolymerization of Tri-n-butyltin Acrylate and Tri-n-butyltin Methacrylate Monomers with Vinyl Monomers Containing Functional Groups

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ABSTRACT

A new approach to obtaining thermoset organotin polymers, which permits control of crosslinking site distribution and, through it, a better control of properties of organotin antifouling polymers, is reported. Tri-n-butyltin acrylate and tri-n-butyltin methacrylate monomers were prepared and copolymerized, by the solution polymerization method with the use of free-radical initiators, with several vinyl monomers containing either an epoxy or a hydroxyl functional group. The reactivity ratios were determined for six pairs of monomers by using the analytical YBR method to solve the differential form of the copolymer equation. For copolymerization of tri-n-butyltin acrylate (M_1) with glycidyl acrylate (M_2), these reactivity ratios were $r_1 = 0.295 \pm 0.053$, $r_2 = 1.409 \pm 0.103$; with glycidyl methacrylate (M_2) they were $r_1 = 0.344 \pm 0.201$, $r_2 = 4.290 \pm 0.273$; and with N-methylolacrylamide (M_2) they

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were $r_1 = 0.977 \pm 0.087$, $r_2 = 1.258 \pm 0.038$. Similarly, for the copolymerization of tri-n-butyltin methacrylate (M_1) with glycidyl acrylate (M_2) these reactivity ratios were $r_1 = 1.356 \pm 0.157$, $r_2 = 0.367 \pm 0.086$; with glycidyl methacrylate (M_2) they were $r_1 = 0.754 \pm 0.128$, $r_2 = 0.794 \pm 0.135$; and with N-methylolacrylamide (M_2) they were $r_1 = 4.230 \pm 0.658$, $r_2 = 0.381 \pm 0.074$. Even though the magnitude of error in determination of reactivity ratios was small, it was not found possible to assign consistent Q,e values to either of the organotin monomers for all of its copolymerizations. Therefore, Q,e values were obtained by averaging all Q,e values found for the particular monomer, and these were Q = 0.852, e = 0.197 for the tri-n-butyltin methacrylate monomer; and Q = 0.235, e = 0.401 for the tri-n-butyltin acrylate monomer. Since the reactivity ratios indicate the distribution of the units of a particular monomer in the polymer chain, the measured values are discussed in relation to the selection of a suitable copolymer which, when crosslinked with appropriate crosslinking agents through functional groups, would give thermoset organotin coatings with an optimal balance of mechanical and antifouling properties.

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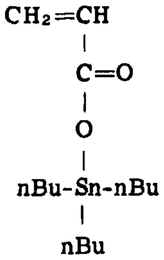
INTRODUCTION

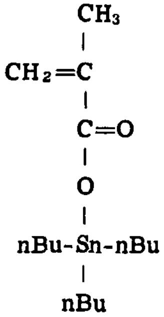
The polymers containing tri-n-butyltin esters of carboxylic acid as side chains have become increasingly important in recent years for control of fouling on ship hulls as well as other surfaces in contact with marine environments. Linear organotin polymers of this type generally have poor physical properties, even though they show acceptable antifouling performance. Our approach to alleviate this problem has been to obtain thermoset, epoxy polymer-based organotin network structures [1-3]. Typically, therefore, the 1:1 copolymer of methyl vinyl ether with maleic anhydride was partially esterified with bis(tri-n-butyltin) oxide, followed by a crosslinking reaction of the free acid or anhydride groups with epoxide monomers. A great improvement in physical properties without any loss of antifouling performance has been achieved by this method. The mechanical properties of the thermosets were controlled mainly by the type and amount of the crosslinking epoxide monomer [2].

To optimize the physical properties and antifouling performance even further, it was desired to control the crosslink site distribution to a much higher degree than is possible in random esterification of polydisperse, linear, carboxylic acid or anhydride-group-containing polymers. With this objective in mind, the copolymerization of tri-n-butyltin acrylate (I) and tri-n-butyltin methacrylate (II) monomers with a number of vinyl monomers containing functional groups was studied [4]. The reactivity ratios and Q,e values were determined for these copolymerization reactions.



$$\begin{array}{c} \mathrm{CH_2{=}CH} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{O} \\ | \\ \mathrm{nBu{-}Sn{-}nBu} \\ | \\ \mathrm{nBu} \end{array}$$

I



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_2{=}C} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{O} \\ | \\ \mathrm{nBu{-}Sn{-}nBu} \\ | \\ \mathrm{nBu} \end{array}$$

II

These values are expected to be very useful in selecting a suitable copolymer for obtaining crosslinked antifouling coatings with optimum physical properties. It should also be noted that although the literature contains many references to polymerization and copolymerization of tri-n-butyltin acrylate and methacrylate with various vinyl monomers to obtain polymers for numerous applications [5-9], there are no reports of reactivity ratios and Q,e values for the copolymerization reactions of these organotin monomers. Finally, organotin compounds are extensively used as UV stabilizers [10, 11]. Therefore, these data should be helpful in incorporation of these two organotin vinyl monomers, for the purpose of UV stabilization, into other vinyl polymers through copolymerization.

THEORETICAL

For the present study, the analytical method of Yezrielev, Brokhina, and Roskin (YBR method) [12], based on the differential form of the copolymer equation, was selected as the most appropriate for calculating reactivity ratios of the free-radical binary vinyl polymerization. In a recent review, Joshi [13] has pointed out that the linear YBR method and the nonlinear Tidwell and Mortimer method (TM method) [14] are the two outstanding present-day methods for calculating reactivity ratios. Of these, the TM method is more accurate in matching copolymer composition, but the YBR method gives a very

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balanced average reactivity ratio in spite of any stray experimental error. Also, the YBR method utilizes a symmetrical form of the copolymer equation which ensures that the reactivity ratios calculated from normal and inverted data are the same. Finally, the YBR theoretical line is situated evenly between the experimental points of positive and negative error. This leads to a determination of reactivity ratios that are kinetically more accurate than those obtainable by the use of the TM method.

The relevant equations for calculating reactivity ratios by the YBR method are given below.

The differential form of the copolymer equation is

$$F_1/F_2 = (f_1/f_2)/[(r_1f_1 + f_2)/(r_2f_2 + f_1)] \tag{1}$$

where $F_1 = 1 - F_2$ = mole fraction of monomer M_1 in the copolymer, $f_1 = 1 - f_2$ = mole fraction of monomer M_1 in the initial monomer mixture, r_1, r_2 = reactivity ratios for monomers M_1 and M_2, respectively, and are defined as the ratios of the rate constants for a given radical adding its own monomer to that for its adding the other monomer. Equation (1) can be rearranged into the YBR equation:

$$\sqrt{kx} - (1/\sqrt{kx}) = r_1 \sqrt{x/k} - r_2 \sqrt{k/x} \tag{2}$$

where

$$x = f_1/f_2 \tag{3}$$

$$k = F_1f_2/F_2f_1 \tag{4}$$

The YBR equation (2) is completely symmetrical with respect to r_1 and r_2. If n experiments corresponding to various compositions of the monomers in the feed are performed, then Eq. (2) can be solved by linear least-squares method to give

$$r_1A_1 - r_2n = C_1 \tag{5}$$

$$-r_1n + r_2A_2 = C_2 \tag{6}$$

where

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$$A_1 = \sum_{i=1}^{n} x_i/k_i \tag{7}$$

$$A_2 = \sum_{i=1}^{n} k_i/x_i \tag{8}$$

$$C_1 = \sum_{i=1}^{n} [x_i - (1/k_i)] \tag{9}$$

$$C_2 = \sum_{i=1}^{n} [(1/x_i) - k_i] \tag{10}$$

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and x_i, k_i are the values of x and k for the i-th experiment.

The solution of Eqs. (5) and (6) gives the expressions for r_1 and r_2:

$$r_1 = (A_2C_1 + nC_2)/(A_1A_2 - n^2) \tag{11}$$

$$r_2 = (A_1C_2 + nC_1)/(A_1A_2 - n^2) \tag{12}$$

Similarly, the mean-square error in the determination of r_1 and r_2 can be calculated as

$$\Delta^2 = \text{mean-square error of the experiment} = \sum_{i=1}^{n} \Delta_i^2/(n - 2) \tag{13}$$

$$\Delta_i^2 = [r_1 \sqrt{x_i/k_i} - r_2 \sqrt{k_i/x_i} - \sqrt{k_ix_i} + (1/\sqrt{k_ix_i})]^2 \tag{14}$$

$$\Delta_{r_1}^2 = \text{mean-square error in determination of } r_1$$

$$= \Delta^2 A_2/(A_1A_2 - n^2) \tag{15}$$

$$\Delta^2_{r_2} = \text{mean-square error in determination of } r_2$$

$$= \Delta^2 A_1/(A_1A_2 - n^2) \tag{16}$$

Combining these equations, we obtain

$$r_1 = [(A_2C_1 + nC_2)/(A_1A_2 - n^2)] \pm \sqrt{\Delta^2 A_2/(A_1A_2 - n^2)} \tag{17}$$

$$r_2 = [(A_1C_2 + nC_1)/(A_1A_2 - n^2)] \pm \sqrt{\Delta^2 A_1/(A_1A_2 - n^2)} \tag{18}$$

The basic procedure employed to calculate reactivity ratios was to solution-copolymerize the organotin monomer with the desired functional-group-containing vinyl monomer using free-radical catalysts. The conversion of the monomers to polymers was limited to less than 10% by trial and error. The copolymer formed was isolated and its composition determined by calculating the amount of tin in the copolymer. When the yield of the copolymer was less than 10%, its composition was taken as approximately equal to an instantaneous composition of the copolymer forming from the initial monomer feed. After carrying out these experiments for a number of compositions of the initial monomer feed, the reactivity ratios were calculated by using Eqs. (17) and (18).

From the reactivity ratios, the Q,e values were calculated by using the Alfrey and Price equations [15]:

$$e_1 = e_2 \pm (-\ln r_1r_2)^{1/2} \tag{19}$$

$$Q_1 = (Q_2/r_2) \exp \{-e_2(e_2 - e_1)\} \tag{20}$$

The Q,e values which represent resonance and polar effects in a monomer and its radical are extensively tabulated by Young [16] from earlier copolymerization data. Thus, by using tabulated Q_2,e_2 values for the functional-group-containing vinyl monomer, the r_1,r_2 values determined in the present study, and setting the product $r_1r_2 = 1$ whenever it is greater than 1, the unknown Q_1,e_1 values for

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the organotin monomer could be calculated by use of Eqs. (19) and (20). These Q_1,e_1 values would be very useful for estimating the reactivity ratios in copolymerization of organotin monomers with a number of vinyl monomers through use of Eqs. (19) and (20).

EXPERIMENTAL

Materials

The epoxy group-containing vinyl monomers, namely, glycidyl methacrylate and glycidyl acrylate, were obtained from the Borden Chemical Co., Philadelphia, Pennsylvania and were purified by vacuum distillation before use. A hydroxyl group-containing vinyl monomer, N-methylolacrylamide, was provided by the American Cyanamid Co., Wayne, New Jersey, as a 60% aqueous solution. It was dried and recrystallized from ethyl acetate to obtain solid crystals of mp 73-74°C before use. The acrylic acid and methacrylic acid monomers were obtained from the Aldrich Chemical Co., Milwaukee, Wisconsin, and used in as-received condition.

The toxicant bis(tri-n-butyltin) oxide was obtained from M & T Chemicals, Rahway, New Jersey, and a free-radical initiator, benzoyl peroxide, was obtained from the Fisher Scientific Co., Fair Lawn, New Jersey, and used in as-received condition. Finally, all solvents used were of reagent grade and obtained from the Mallinckrodt Chemical Co., St. Louis, Missouri.

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Preparation of Organotin Monomers

The tri-n-butyltin methacrylate and tri-n-butyltin acrylate monomers were prepared according to the method of Montermoso et al. [7]. The experimental procedures used are described below.

Tri-n-butyltin Methacrylate. A 103.8-g portion (0.174 mole) of bis(tri-n-butyltin) oxide was added to 300 ml benzene in a 1-liter three-necked flask. Next, 30 g (0.348 mole) methacrylic acid was added very slowly to the solution while cooling down the flask to maintain reaction mixture temperature to below 25° C. After acid addition, the flask was placed in a heating mantle and provided with an azeotropic distillation head connected to a reflux condenser, a thermometer to read reaction solution temperature, and a dropping funnel with benzene. The solution was stirred with a magnetic stirrer and pump vacuum applied. The heating rate and the vacuum were so adjusted that the reaction solution refluxed at 30°C for 4 hr, at the end of which 3.1 ml of water had been collected in the azeotropic distillation head. The reaction solution was now transferred to another flask and benzene removed with the aid of a rotary evaporator, while taking precaution that the reaction solution temperature never rose to higher than 30°C. Spontaneous polymerization of this monomer occurred if the temperature was allowed to rise above 30°C. The resulting pale yellow viscous liquid was diluted with 150 ml petroleum ether and then cooled to -20°C. This temperature was maintained for 2 hr, at the end of which the product separated as long, thick, transparent crystals, having a melting point of 18.1-18.3°C (lit. [7] mp, 18°C). The tin content of this product was determined by gravimetry through oxidation of a sample to tin oxide using sulfuric acid and a few drops of nitric acid in accordance with the Gilman and Rosenberg method [17]. The tin content (Sn) was found to be 31.4%, against a calculated value of 31.7% for tri-n-butyltin methacrylate monomer. The yield approached the stoichiometric value.

Tri-n-butyltin Acrylate. The procedure for preparing this monomer was similar to the one described above except that it was not necessary to maintain a low temperature. Thus 25.1 g (0.348 mole) of acrylic acid and 103.8 g (0.174 mole) of bis(tri-n-butyltin) oxide were mixed together in 300 ml benzene. The reaction solution was heated to reflux at atmospheric pressure. The refluxing was continued for 4 hr, at the end of which 3.0 ml of water had been collected in the azeotropic distillation head. Solvent benzene was now removed with the aid of a rotary evaporator and the resulting product purified by crystallization from petroleum ether. The tri-n-butyltin acrylate monomer separated out as needlelike crystals having a melting point of 74.0-74.5°C (lit. [7] mp 74.5-75°C). The tin content (Sn) was found to be 32.7% against a calculated value of 32.9%. The yield was almost stoichiometric.

Copolymerization

The copolymers were obtained by the solution polymerization method with the use of benzoyl peroxide as a free-radical initiator. A suitable solvent for carrying out the copolymerization reaction and a nonsolvent for isolating the copolymer from its monomers were determined initially by trial and error for every copolymer. Since the differential form of the copolymer equation was to be used for calculating reactivity ratios, it was necessary to limit

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conversion to less than 10% in every case, again by trial and error. The composition of the copolymer obtained, when the yield was less than 10%, was calculated by determining its tin content through oxidation of the sample to tin oxide. The ratios of monomers in the initial reaction mixture were varied over as wide a range as possible, and the corresponding approximate instantaneous compositions of the copolymers formed were determined. The individual copolymerization procedures are described below.

Copolymerization of Tri-n-butyltin Acrylate with Glycidyl Methacrylate and with Glycidyl Acrylate. Predetermined amounts of tri-n-butyltin acrylate and glycidyl methacrylate (or glycidyl acrylate) were charged into a small glass bottle and benzene, as solvent, was added to obtain a concentration of total monomer equal to 1.57 mole/liter of solution. The solution was next flushed with nitrogen for 10 min, and benzoyl peroxide (1 mole % based on total monomer moles in solution) was added as a free-radical initiator. The bottle was capped with a serum stopper and placed in a constant-temperature oil bath maintained at 75 ± 0.1°C. Vapors produced from the reaction solution and expanded air were allowed to escape with the help of a syringe needle inserted through the stopper. After 5 min, when the temperatures of the reaction solution and the oil bath were in equilibrium, the syringe needle was removed. The polymerization was allowed to proceed and, after some known time interval, when a slight change in viscosity was observed, the bottle was taken out of the oil bath and its contents poured into a beaker containing 200 ml methanol. The copolymer formed precipitated out, while the unreacted monomers remained in solution. The precipitate was isolated by centrifugation, washed with fresh methanol, dried under vacuum, and weighed. If the copolymer yield was more than 10%, the experiment was disregarded and a repeat run was made for a shorter period of time. If the copolymer yield was less than 10%, the composition of the copolymer was calculated by determining its tin content.

The tin content was determined through oxidation of the sample to tin oxide according to the method of Gilman and Rosenberg [17]. Thus, approximately 0.2 g of the organotin copolymer sample was placed in a 30-ml fused silica crucible. To this were added, with caution, 3 ml of concentrated sulfuric acid and 3-5 drops of nitric acid. The crucible was heated slowly over a flame until the sample turned black, and then cautious heating was maintained until the excess acid was removed. Subsequently, the carbonaceous material formed by the action of the acid was completely calcined for 1 hr over high heat, leaving the stannic oxide as a pale yellow solid residue.

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From the weight of this residue, the tin content of the copolymer sample was calculated and the copolymer composition determined.

Copolymerization of Tri-n-butyltin Methacrylate with Glycidyl Methacrylate and with Glycidyl Acrylate. Since tri-n-butyltin methacrylate is liquid at room temperature, it was not necessary to add benzene to obtain a homogeneous solution. Use of benzene was also precluded by the fact that it was insoluble in the precipitant to be used to isolate the copolymer. The copolymerization was conducted at 75 ± 0.1°C, and the procedure was exactly the same as described above. A methanol-water mixture was used to precipitate the copolymer from the reaction solution.

Copolymerization of N-methylolacrylamide with Tri-n-butyltin Methacrylate and with Tri-n-butyltin Acrylate. The temperature of copolymerization was reduced to 65 ± 0.1°C because the copolymerization of these pairs of monomers proceeded too rapidly at 75°C. Methanol was used as the reaction medium, and the copolymerization procedure was the same as described above. The method of isolating the copolymer was to pour the reaction mixture into water. The precipitate, which was free of N-methylolacrylamide monomer, was separated, dried, and redissolved in methanol. Benzene was next added to this solution to isolate the copolymer, free of its monomers, as a precipitate.

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RESULTS AND DISCUSSION

Organotin Monomers

The infrared spectra of the tri-n-butyltin acrylate and tri-n-butyltin methacrylate monomers were recorded by using a Perkin-Elmer model 621 grating infrared spectrophotometer and are shown in Figs. 1 and 2, respectively. The more characteristic peaks of these spectra are the ones corresponding to the $-COOSn\equiv$ group at 1640 cm^{-1} and at 1580 cm^{-1}. The 1640 cm^{-1} peak, which is most characteristic of the $-COOSn\equiv$ group, was determined by comparing the infrared spectrum of a linear polymer containing carboxylic acid groups (1:1 copolymer of methyl vinyl ether with maleic acid) with the infrared spectrum of the same linear polymer after complete esterification with bis(tri-n-butyltin) oxide. However, in the present case, the 1640 cm^{-1} peak superimposes on the absorbance for vinyl double bonds.

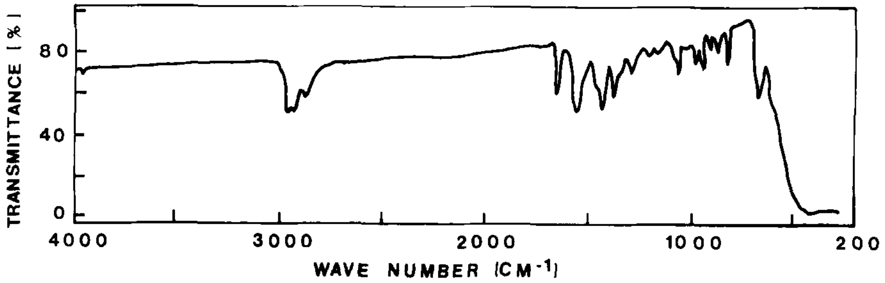

FIG. 1. Infrared spectrum of tri-n-butyltin acrylate monomer.

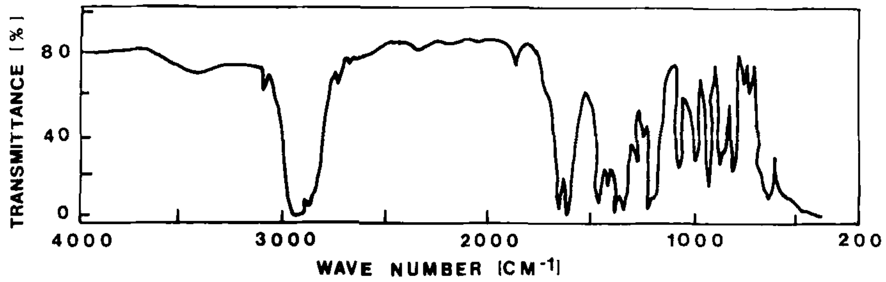

FIG. 2. Infrared spectrum of tri-n-butyltin methacrylate monomer.

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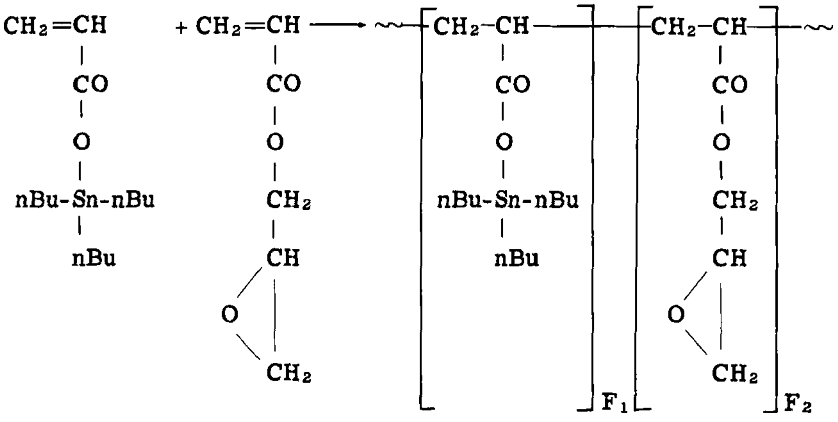
Both monomers are soluble in most organic solvents. The tri-n-butyltin methacrylate monomer polymerizes spontaneously in the absence of added catalysts at temperatures higher than 30° C to give an elastomeric product that is insoluble in methanol. However, in the absence of added catalysts, the tri-n-butyltin acrylate monomer homopolymerizes, only with difficulty, upon long exposures to temperatures much higher than 30° C.

Reactivity Ratios in Copolymerization of Tri-n-butyltin Acrylate (M_1) with Glycidyl Acrylate (M_2)

The copolymerization of tri-n-butyltin acrylate with glycidyl acrylate can be represented by Eq. (21).

Table 1 gives the experimental conditions and results of the



MW = 360.7 MW = 128 (21)

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copolymerization of tri-n-butyltin acrylate (monomer M_1) with glycidyl acrylate (monomer M_2). In this table the instantaneous copolymer composition is tabulated as a function of the composition of the initial monomer mixture. Thus f_1, f_2 are mole fractions of monomers M_1,M_2 in the initial monomer mixture excluding other components, and F_1,F_2 are mole fractions of the units of monomers M_1,M_2 in the copolymer. The copolymer composition was calculated from the tin content of the copolymer as follows:

A material balance for tin in reactants and products can be expressed as

$$W_C \, X_{SC} = W_C \, N \, X_{SE} + W_C \, (1 - N) \, X_{SG} \tag{22}$$

where N, 1 - N = weight fractions of M_1 and M_2 monomer units in the copolymer, respectively, W_C = weight of copolymer sample, and X_{SC}, X_{SE}, X_{SG} = % Sn by weight in the copolymer and the monomers M_1 and M_2 respectively. Rearranging terms and observing that X_{SG} = 0 (i.e., no tin in monomer M_2), we obtain

$$N = X_{SC}/X_{SE}$$

$$= \%\text{ Sn in copolymer}/\%\text{Sn in monomer } M_1 \tag{23}$$

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TABLE 1. Copolymerization of Tri-n-butyltin Acrylate (M_1) with Glycidyl Acrylate (M_2)[a]

Initial monomer mixture		Copolymer yield, % by wt of monomers	Tin content of copolymer % by wt	Copolymer composition	
Mole fraction of M_1, f_1	Mole fraction of M_2, f_2			Mole fraction of M_1, F_1	Mole fraction of M_2, F_2
0.10	0.90	3.73	5.80	0.0758	0.9242
0.20	0.80	10.50	10.23	0.1380	0.8620
0.30	0.70	9.80	12.80	0.1843	0.8159
0.40	0.60	10.20	15.48	0.2397	0.7603
0.50	0.50	1.46	18.08	0.3021	0.6979
0.60	0.40	9.70	21.50	0.4009	0.5991
0.70	0.30	9.90	25.80	0.5632	0.4368
0.80	0.20	8.90	27.95	0.6671	0.3329
0.90	0.10	9.70	29.53	0.7567	0.2433

[a] Polymerization conditions: solvent, benzene; total monomer concentration ($[M_1] + [M_2]$), 1.57 mole/liter; catalyst, benzoyl peroxide (1 mole % of monomers); temperature, 75 ± 0.1°C; copolymer isolation method, precipitation with methanol.

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TABLE 2. Illustration of the Calculation Scheme for Determining r_1, r_2 by the YBR Method: Copolymerization of Tri-n-butyltin Acrylate (M_1) with Glycidyl Acrylate (M_2)

$k_i = \frac{F_1 f_2}{F_2 f_1}$	$x_i = \frac{f_1}{f_2}$	$\frac{x_i}{k_i}$	$\frac{k_i}{x_i}$	$x_i - \frac{1}{k_i}$	$\frac{1}{x_i} - k_i$	$(\frac{x_i}{k_i})^{1/2}$	$(\frac{k_i}{x_i})^{1/2}$	$(k_i x_i)^{1/2}$	$\frac{1}{(k_i \cdot x_i)^{1/2}}$	Δ_i^2
0.7381	0.1111	0.1505	6.6436	-1.2437	8.2619	0.3879	2.5775	0.2862	3.4937	0.0952
0.6404	0.2500	0.3904	2.5616	-1.3116	3.3596	0.6248	1.6005	0.4001	2.4992	0.0008
0.5272	0.4286	0.8129	1.2301	-1.4682	1.8061	0.9016	1.1091	0.4753	2.1037	0.1104
0.4729	0.6667	1.4098	0.7093	-1.4479	1.0271	1.1874	0.8422	0.5615	1.7809	0.1472
0.4329	1.0000	2.3100	0.4329	-1.3102	0.5671	1.5199	0.6579	0.6579	1.5199	0.1475
0.4461	1.5000	3.3625	0.2974	-0.7416	0.2206	1.8337	0.5453	0.8180	1.2225	0.0316
0.5526	2.3333	4.2224	0.2368	0.5236	-0.1240	2.0548	0.4866	1.1355	0.8807	0.1112
0.5009	4.0000	7.9856	0.1252	2.0039	-0.2509	2.8259	0.3539	1.4155	0.7065	0.1391
0.3456	9.0000	26.0417	0.0384	6.1063	-0.2345	5.1031	0.1959	1.7636	0.5670	0.0012
	Σ =	46.6858	12.2753	1.1106	14.6330					0.7842
		$= A_1$	$= A_2$	$= C_1$	$= C_2$					$= \Sigma \Delta_i^2$

$$r_1 = \frac{(12.2753)(1.1106) + 9\ (14.6330)}{(46.6858)(12.2753) - 9^2} = 0.295; \quad r_2 = \frac{(46.6858)(14.6330) + 9(1.1106)}{(46.6858)(12.2753) - 9^2} = 1.409$$

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$$\Delta_1^2 = [(0.295)(0.3879) - (1.409)(2.5775) - 0.2862 - 3.4937]^2 = 0.0952;\ \Delta^2 = \frac{0.7842}{9 - 2} = 0.1120$$

$$\Delta r_1 = \left(\frac{(0.1120)(12.753)}{(46.6858)(12.2753) - 9^2}\right)^{1/2} = 0.053 \qquad \Delta r_2 = \left(\frac{(0.1120)(46.6858)}{(46.6858)(12.2753) - 9^2}\right)^{1/2} = 0.1031$$

Thus $r_1 = 0.295 \pm 0.053$, $r_2 = 1.409 \pm 0.103$

Therefore, the mole fraction F_1 is given by

$$F_1 = \frac{N/\text{mol. wt. of } M_1}{(N/\text{mol. wt. of } M_1) + [(1 - N)/\text{mol. wt. of } M_2]} \tag{24}$$

and

$$F_2 = 1 - F_1 \tag{25}$$

Thus, by using the experimental data given in Table 1 and on applying Eqs. (7)-(18) of the analytical YBR method, the reactivity ratios of monomer tri-n-butyltin acrylate (M_1) with monomer glycidyl acrylate (M_2) were calculated to be

$$r_1 = 0.295 \pm 0.053$$

$$r_2 = 1.409 \pm 0.103$$

An illustration of the calculation scheme is given in Table 2. The experimental errors in r_1 and r_2 are within a small range and, therefore, these values are of excellent reliability, as can also be judged from Fig. 3. In this figure, the theoretical copolymer composition curve, F_1 vs. f_1, is plotted by generating F_1 vs. f_1 data from calculated r_1 and r_2 values and Eq. (1). In the same figure, the experimental F_1 vs. f_1 values from Table 1 are also plotted and, as can be seen, the theoretical curve closely represents the experimental data. Finally, since r_2 is high compared to 1, the resulting copolymer should contain blocks of glycidyl acrylate units.

Reactivity Ratios in Copolymerization of Tri-n-butyltin Acrylate (M_1) with Glycidyl Methacrylate (M_2)

The experimental conditions and results of copolymerization of tri-n-butyltin acrylate with glycidyl methacrylate are given in Table 3. As before, the reactivity ratios for this pair of monomers were calculated to be

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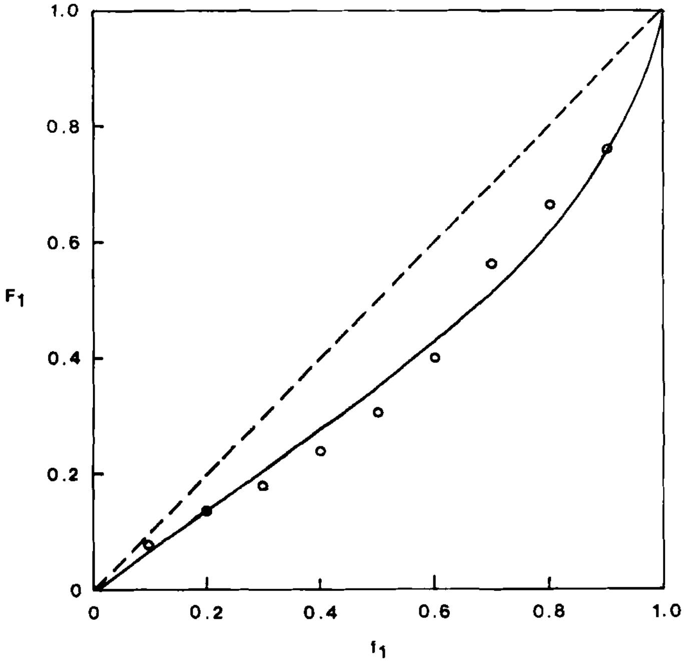

FIG. 3. Copolymer-initial monomer mixture composition for the copolymerization of tri-n-butyltin acrylate (M_1) with glycidyl acrylate (M_2): (o) experimental values; (—) curve calculated from the copolymer equation using reactivity ratios determined by the YBR method for this system. F_1 and f_1 are mole fractions of M_1 in the copolymer and in the initial monomer mixture, respectively.

$r_1 = 0.344 \pm 0.201$

$r_2 = 4.290 \pm 0.273$

Figure 4 shows the matching of experimental data with the theoretical curve determined by using calculated r_1,r_2 values. The rates of copolymerization for this pair of monomers dropped sharply at $f_1 > 0.5$ and hence the copolymer composition data for $f_1 > 0.5$ were not obtained.

Since $r_2 \gg 1$ in this case, the copolymer of tri-n-butyltin acrylate

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TABLE 3. Copolymerization of Tri-n-butyltin Acrylate (M_1) with Glycidyl Methacrylate (M_2)[a]

Initial monomer mixture		Copolymer yield, % by wt of monomers	Tin content of copolymer, % by wt	Copolymer composition	
Mole fraction of M_1, f_1	Mole fraction of M_2, f_2			Mole fraction of M_1, F_1	Mole fraction of M_2, F_2
0.10	0.90	10.2	2.00	0.0248	0.9752
0.20	0.80	8.1	4.46	0.0582	0.9418
0.30	0.70	6.5	7.60	0.1057	0.8943
0.35	0.65	8.1	7.96	0.1116	0.8884
0.40	0.60	9.5	9.32	0.1346	0.8654

[a] Polymerization conditions: solvent, benzene; total monomer concentration ($[M_1] + [M_2]$), 1.57 mole/liter; catalyst, benzoyl peroxide (1 mole % of monomers); temperature, 75 ± 0.1°C; copolymer isolation method, precipitation with methanol.

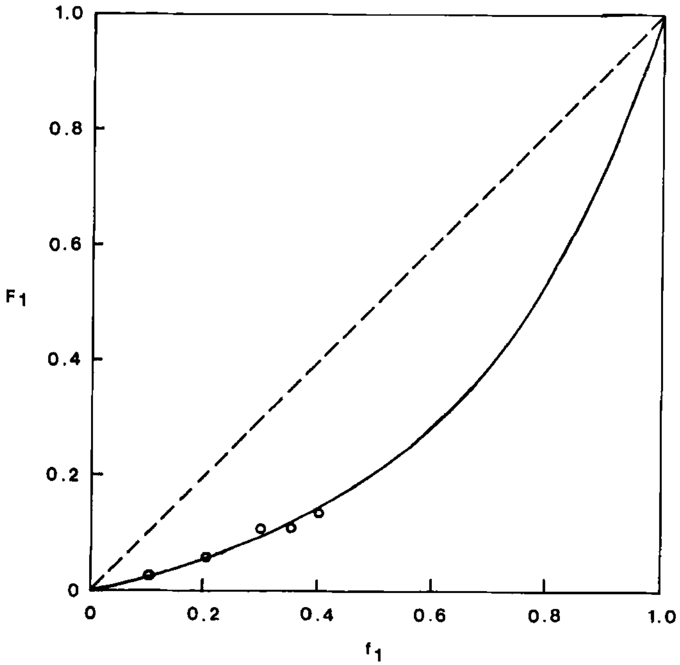

FIG. 4. Copolymer-initial monomer mixture composition for the copolymerization of tri-n-butyltin acrylate (M_1) with glycidyl methacrylate (M_2): (○) experimental values; (—) curve calculated from the copolymer equation using reactivity ratios determined by the YBR method for this system. F_1 and f_1 are mole fractions of M_1 in the copolymer and in the initial monomer mixture, respectively.

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with glycidyl methacrylate will contain large blocks of glycidyl methacrylate units. Also, since the glass transition temperature of glycidyl methacrylate homopolymer is much higher than that of the corresponding homopolymer of tri-n-butyltin acrylate, the copolymer should behave like a reinforced elastomer.

Reactivity Ratios in Copolymerization of Tri-n-butyltin Acrylate (M_1) with N-Methylolacrylamide (M_2)

Because the solubility characteristics of tri-n-butyltin acrylate are very different from those of N-methylolacrylamide monomer,

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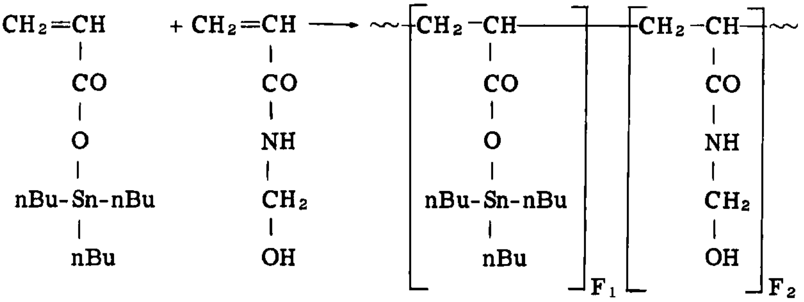
it was found difficult to locate a suitable reaction medium. None of the solvents or solvent mixtures tried gave a homogeneous single-phase reaction solution over the entire range of compositions of the initial monomer mixture. The best results were obtained with methanol, which gave a single-phase reaction solution for values of mole fraction f_1 of tri-n-butyltin acrylate in the initial monomer mixture varying between 0 and 0.5. Beyond an f_1 value of 0.5, a second phase appeared by the precipitation of the copolymer formed during the reaction, thus invalidating the use of the copolymer equation for data corresponding to $f_1 > 0.5$.



$$\begin{array}{c} CH_2{=}CH \\ | \\ CO \\ | \\ O \\ | \\ nBu\text{-}Sn\text{-}nBu \\ | \\ nBu \end{array} + \begin{array}{c} CH_2{=}CH \\ | \\ CO \\ | \\ NH \\ | \\ CH_2 \\ | \\ OH \end{array} \longrightarrow \sim\!\sim\left[\begin{array}{c} CH_2-CH \\ | \\ CO \\ | \\ O \\ | \\ nBu\text{-}Sn\text{-}nBu \\ | \\ nBu \end{array}\right]_{F_1}\left[\begin{array}{c} CH_2-CH \\ | \\ CO \\ | \\ NH \\ | \\ CH_2 \\ | \\ OH \end{array}\right]_{F_2}\sim\!\sim \qquad (26)$$

The method of separating the copolymer from its monomers, selected after much trial and error, was to pour the reaction mixture in water, which precipitated the copolymer and unreacted tri-n-butyltin acrylate monomer leaving behind N-methylolacrylamide monomer in solution. Next the precipitate was recovered, washed with fresh water, and redissolved in methanol. Benzene was then added to this solution to precipitate the copolymer which was isolated, dried and its composition determined by tin analysis.

Table 4 shows the experimental conditions and the results of the copolymerization of tri-n-butyltin acrylate with N-methylolacrylamide. From these data the monomer reactivity ratios were computed by using the YBR method as discussed above. These ratios were found to be

$$r_1 = 0.977 \pm 0.087$$

$$r_2 = 1.258 \pm 0.038$$

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TABLE 4. Copolymerization of Tri-n-butyltin Acrylate (M_1) with N-Methylolacrylamide (M_2)[a]

Initial monomer mixture		Copolymer yield, % by wt of monomers	Tin content of copolymer, % by wt	Copolymer composition	
Mole fraction of M_1, f_1	Mole fraction of M_2, f_2			Mole fraction of M_1, F_1	Mole fraction of M_2, F_2
0.10	0.90	9.20	8.0	0.0825	0.9175
0.20	0.80	7.00	14.0	0.1718	0.8282
0.30	0.70	11.10	18.2	0.2574	0.7426
0.40	0.60	9.50	22.5	0.3772	0.6228
0.50	0.50	6.80	24.8	0.4616	0.5384

[a] Polymerization conditions: solvent, methanol; total monomer concentration ($[M_1] + [M_2]$), 0.28 mole/liter; catalyst, benzoyl peroxide (1 mole % of monomers); temperature, 65 ± 0.1°C; copolymer isolation method, precipitation with water, followed by redissolution in methanol and reprecipitation with benzene.

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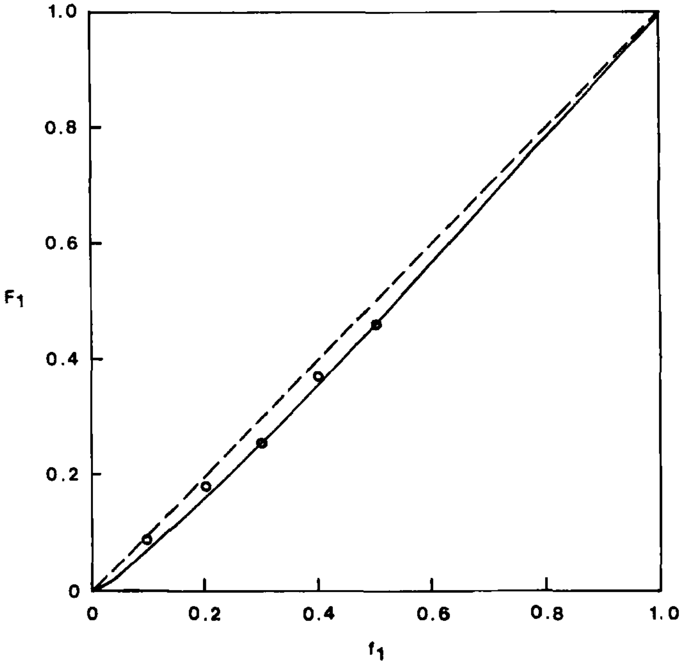

FIG. 5. Copolymer-initial monomer mixture composition for the copolymerization of tri-n-butyltin acrylate (M_1) with N-methylolacrylamide (M_2): (○) experimental values; (—) curve calculated from the copolymer equation using reactivity ratios determined by the YBR method for this system. F_1 and f_1 are mole fractions of M_1 in the copolymer and in the initial monomer mixture, respectively.

Figure 5 shows the match between computed F_1 vs. f_1 curve and experimental F_1 vs. f_1 data. Finally, in the present case, since $r_1 = r_2 \cong 1$, a random distribution of the units of N-methlolacrylamide and tri-n-butyltin acrylate along the copolymer chain can be expected.

Reactivity Ratios in Copolymerization of Tri-n-butyltin Methacrylate (M_1) with Glycidyl Acrylate (M_2)

Because of the difficulties in devising a suitable method of separating this copolymer from its monomers, and the fact that tri-n-butyltin

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methacrylate and glycidyl acrylate monomers are liquid at room temperature and completely miscible with each other, it was decided to conduct the copolymerization reaction in the absence of added solvents. The copolymer was separated from its monomers by precipitation using a methanol-water mixture (80:20 by volume) as nonsolvent.

The conditions and results of experiments for the copolymerization of this pair of monomers are given in Table 5. The corresponding values of the reactivity ratios were calculated to be

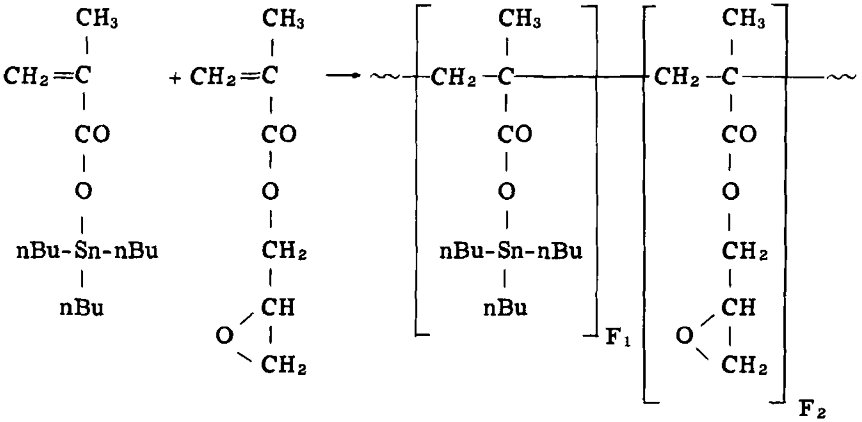
$$r_1 = 1.356 \pm 0.157$$

$$r_2 = 0.367 \pm 0.086$$

By using these values of r_1 and r_2, the copolymer composition curve F_1 vs. f_1 was calculated and is shown in Fig. 6 along with the experimental data. Since $r_1 > 1$, the copolymer would be expected to contain blocks of tri-n-butyltin methacrylate units along the chain.

Reactivity Ratios in Copolymerization of Tri-n-butyltin Methacrylate (M_1) with Glycidyl Methacrylate (M_2)

The conditions and results of experiments for the copolymerization of this pair of monomers [Eq. (27)] are given in Table 6. The



$$CH_2{=}C(CH_3)\text{-}CO\text{-}O\text{-}Sn(nBu)_3 + CH_2{=}C(CH_3)\text{-}CO\text{-}O\text{-}CH_2\text{-}\underset{O}{CH\text{-}CH_2} \longrightarrow \sim\left[CH_2\text{-}C(CH_3)(CO\text{-}O\text{-}Sn(nBu)_3)\right]_{F_1}\left[CH_2\text{-}C(CH_3)(CO\text{-}O\text{-}CH_2\text{-}\underset{O}{CH\text{-}CH_2})\right]_{F_2}\sim$$

(27)

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TABLE 5. Copolymerization of Tri-n-butyltin Methacrylate (M_1) with Glycidyl Acrylate (M_2)[a]

Initial monomer mixture		Copolymer yield, % by wt of monomers	Tin content of copolymer, % by wt	Copolymer composition	
Mole fraction of M_1, f_1	Mole fraction of M_2, f_2			Mole fraction of M_1, F_1	Mole fraction of M_2, F_2
0.10	0.90	8.60	14.45	0.22	0.78
0.20	0.80	10.20	18.62	0.33	0.67
0.31	0.69	10.34	22.58	0.46	0.54
0.40	0.60	10.50	25.20	0.58	0.42
0.50	0.50	8.50	26.80	0.66	0.34
0.60	0.40	5.67	28.04	0.73	0.27
0.70	0.30	9.20	28.30	0.73	0.27
0.80	0.20	13.65	28.89	0.82	0.18
0.90	0.10	7.00	31.20	0.94	0.06

[a] Polymerization conditions: solvent, none; catalyst, benzoyl peroxide (1 mole % of monomers); temperature, 75 ± 0.1°C; copolymer isolation method, precipitation with methanol-water mixture (80:20 by volume).

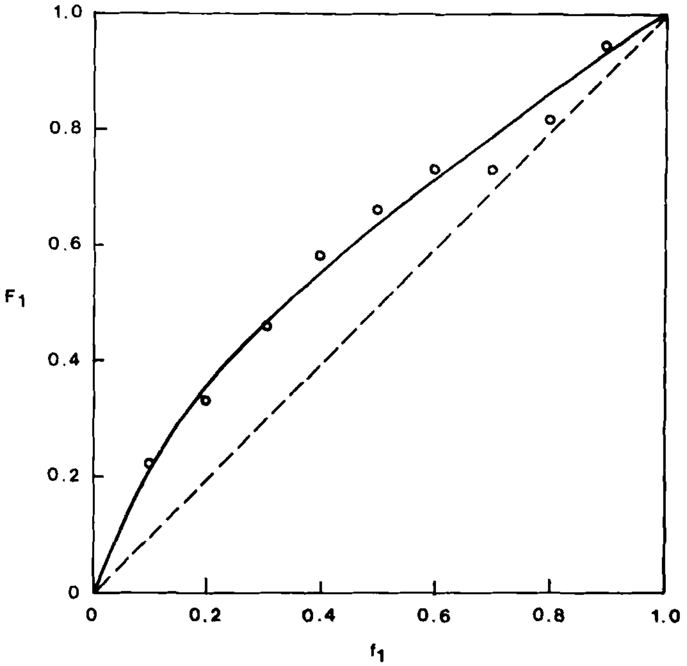

FIG. 6. Copolymer-initial monomer mixture composition for the copolymerization of tri-n-butyltin methacrylate (M_1) with glycidyl acrylate (M_2): (○) experimental values; (—) curve calculated from the copolymer equation using reactivity ratios determined by the YBR method for this system. F_1 and f_1 are mole fractions of M_1 in the copolymer and in the initial monomer mixture, respectively.

corresponding values of the reactivity ratios, calculated by using the YBR method, were found to be

$$r_1 = 0.754 \pm 0.128$$

$$r_2 = 0.794 \pm 0.135$$

Since both r_1 and $r_2 < 1$, the copolymer would be expected to contain a significant amount of alternating monomer unit sequences along the polymer chain.

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TABLE 6. Copolymerization of Tri-n-butyltin Methacrylate (M_1) with Glycidyl Methacrylate (M_2)[a]

Initial monomer mixture		Copolymer yield, % by wt of monomers	Tin content of copolymer, % by wt	Copolymer composition	
Mole fraction of M_1, f_1	Mole fraction of M_2, f_2			Mole fraction of M_1, F_1	Mole fraction of M_2, F_2
0.10	0.90	11.10	7.46	0.1044	0.8956
0.20	0.80	2.40	14.29	0.2373	0.7627
0.30	0.70	5.35	16.85	0.3007	0.6993
0.40	0.60	9.13	20.40	0.4062	0.5938
0.50	0.50	2.83	25.97	0.6320	0.3680
0.60	0.40	10.60	25.79	0.6233	0.3767
0.70	0.30	7.52	27.16	0.6939	0.3061
0.80	0.20	8.50	27.01	0.7033	0.2967
0.90	0.10	10.80	30.29	0.8905	0.1095

[a] Polymerization conditions: solvent, none; catalyst, benzoyl peroxide (1 mole % of monomers); temperature, 75 ± 0.1°C; copolymer isolation method, precipitation with methanol-water mixture (80:20 by volume).

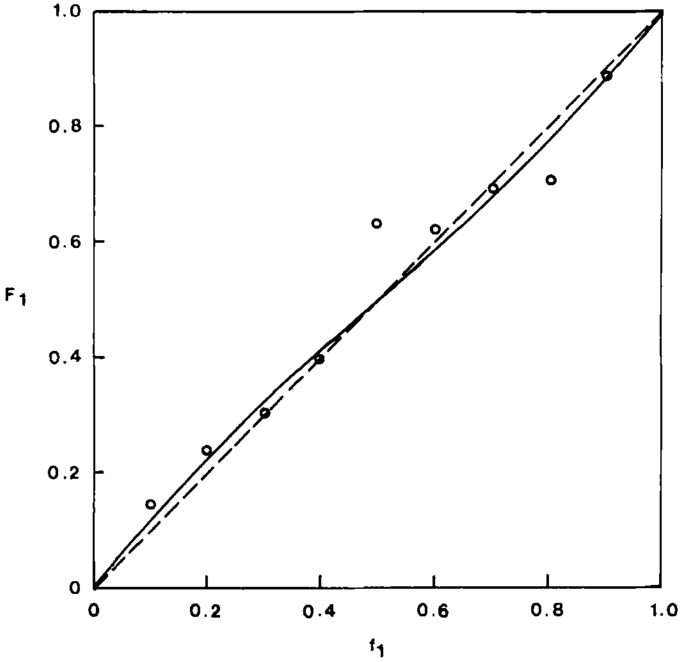

FIG. 7. Copolymer-initial monomer mixture composition for the copolymerization of tri-n-butyltin methacrylate (M_1) with glycidyl methacrylate (M_2): (○) experimental values; (—) curve calculated from the copolymer equation using reactivity ratios determined by the YBR method for this system. F_1 and f_1 are mole fractions of M_1 in the copolymer and in the initial monomer mixture, respectively.

Using the calculated r_1 and r_2 values and Eq. (1), the theoretical copolymer composition curve, F_1 vs. f_1, was calculated and is shown in Fig. 7 along with the experimental data. As can be seen, most experimental points agree with the theoretical curve, but the points at $f_1 = 0.5$ and 0.8 deviate significantly from the theoretical curve. Further, the points in the region $f_1 = 0.5$ to 0.8 fall on a plateau. This suggests that the terminal model of binary copolymerization, on which Eq. (1) is based, is probably not valid for the present copolymerization reaction. Existence of a plateau region in the F_1 vs. f_1 experimental data strongly indicates the participation of the charge transfer complex between the two monomers in copolymerization.

The theoretical curve F_1 vs. f_1 crosses the line representing

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$F_1 = f_1$ as expected, since both r_1 and r_2 are less than unity. The intersection point represents the azeotropic composition, i.e., the composition at which the copolymer has the same composition as the composition of monomers in the initial monomer mixture. This composition can also be calculated by substituting $F_1 = f_1$ in Eq. (1):

$$(f_1)_{\text{azeotropic}} = (1 - r_2)/(2 - r_1 - r_2)$$

$$= 0.46 \text{ for the present case.} \qquad (28)$$

Reactivity Ratios in Copolymerization of Tri-n-butyltin Methacrylate (M_1) with N-Methylolacrylamide (M_2)

The copolymerization behavior of this pair of monomers was very similar to the tri-n-butyltin acrylate-N-methylolacrylamide pair. The reaction medium was methanol, and the copolymer was separated from its monomers by precipitation with water followed by reprecipitation by benzene. Also, the homogeneous single-phase copolymerization occurred only when f_1 was less than 0.5. Above this value the copolymer formed precipitated out during reaction.

Table 7 shows the experimental conditions and results of copolymerization of tri-n-butyltin methacrylate with N-methylolacrylamide. Based on these data, the reactivity ratios were calculated to be

$$r_1 = 4.230 \pm 0.658$$

$$r_2 = 0.381 \pm 0.074$$

Figure 8 shows the theoretical F_1 vs. f_1 curve based on these reactivity ratios as well as the experimental F_1 vs. f_1 data. Since $r_1 \gg 1$, the copolymer will have blocks of tri-n-butyltin methacrylate units.

Q,e Values in Copolymerization of Tri-n-butyltin Acrylate and Tri-n-butyltin Methacrylate Monomers with Various Vinyl Monomers

The Q,e scheme is very useful in estimating the reactivity ratios for the copolymerization of monomers for which no experimental reactivity ratio data exist. Thus the Q,e values for tri-n-butyltin

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TABLE 7. Copolymerization of Tri-n-butyltin Methacrylate (M_1) with N-Methylolacrylamide (M_2)[a]

Initial monomer mixture		Copolymer yield, % by wt of monomers	Tin content of copolymer, % by wt	Copolymer composition	
Mole fraction of M_1, f_1	Mole fraction of M_2, f_2			Mole fraction of M_1, F_1	Mole fraction of M_2, F_2
0.10	0.90	10.10	17.50	0.2494	0.7506
0.23	0.77	9.70	24.30	0.4695	0.5305
0.30	0.70	10.50	27.40	0.6320	0.3680
0.40	0.60	2.52	28.18	0.6833	0.3167
0.50	0.50	7.90	29.75	0.8044	0.1956

[a] Polymerization conditions: solvent, methanol; total monomer concentration ($[M_1] + [M_2]$); 0.28 mole/liter; catalyst: benzoyl peroxide (1 mole % of monomers); temperature, 65 ± 0.1°C; copolymer isolation method, precipitation with water, followed by redissolution in methanol and reprecipitation with benzene.

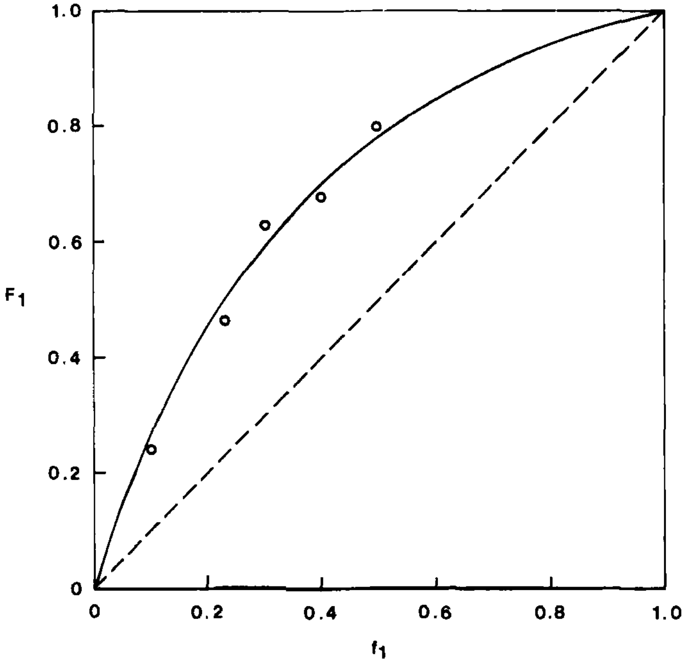

FIG. 8. Copolymer-initial monomer mixture composition for the copolymerization of tri-n-butyltin methacrylate (M_1) with N-methylol-acrylamide (M_2): (o) experimental values; (—) curve calculated from the copolymer equation using reactivity ratios determined by the YBR method for this system. F_1 and f_1 are mole fractions of M_1 in the copolymer and in the initial monomer mixture, respectively.

acrylate and tri-n-butyltin methacrylate monomers were obtained by using the Alfrey-Price equations (19, 20) and the reactivity ratio data discussed in earlier sections. The Q_2,e_2 values for the vinyl comonomers were obtained from the compilation by Young [16]. As is the usual practice, the product r_1r_2 was set equal to 1 whenever it was greater than 1 so that Eq. (19) could be solved. The results are summarized in Table 8. It is apparent from Table 8 that no Q_1,e_1 values could be assigned to either tri-n-butyltin acrylate or tri-n-butyltin methacrylate monomers which would be consistent for all of the copolymerization reactions of each monomer. This is in spite of the fact that error in determination of reactivity ratios itself is small. Under the circumstances, averages of Q_1,e_1 values which match most closely with each other for each of the organotin monomers

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TABLE 8. Q,e Values in Copolymerization of Organotin Monomers with Vinyl Monomers

						Average	
Monomer M_1	Monomer M_2	Q_2^a	e_2^a	Q_1	e_1	Q_1	e_1
Tri-n-butyltin acrylate	Glycidyl acrylate	0.55	0.96	0.961	1.896		
				0.156^c	0.024^c		
	Glycidyl methacrylate	1.03	0.57	0.240^b	0.570^b	0.235	0.401
	N-Methylolacrylamide	0.39	0.61	0.310^b	0.610^b		
Tri-n-butyltin methacrylate	Glycidyl acrylate	0.55	0.96	3.316^c	1.791^c		
				0.669	0.129		
	Glycidyl methacrylate	1.03	0.57	0.863	-0.147	0.852	0.197
				1.959^c	1.287^c		
	N-Methylolacrylamide	0.39	0.61	1.024^b	0.610^b		

[a] Q_2, e_2 values from Young [16].

[b] In calculating these values, the product $r_1 r_2$ was found to be >1 and was thus set equal to 1.

[c] These values were excluded from calculation of average Q_1, e_1 as being inconsistent with other Q_1, e_1 values for the particular organotin monomer.

were obtained. These average Q_1,e_1 values for tri-n-butyltin acrylate and tri-n-butyltin methacrylate monomers are very comparable to the Q,e values reported in the literature [16] for other esters of acrylic and methacrylic acids.

SUMMARY AND CONCLUSIONS

The importance of crosslinking reactions in improving mechanical properties of antifouling coatings, without a significant reduction in antifouling effectiveness, has been well established in our earlier investigations. In the research reported here, a different approach to obtaining thermoset organotin antifouling polymers, which permits a control of the distribution of crosslinking sites and hence a much better control of the physical properties of the resulting polymers, was explored in detail. Thus, tri-n-butyltin acrylate and tri-n-butyltin methacrylate monomers were copolymerized, by solution polymerization using free-radical initiators as catalysts, with vinyl monomers containing a crosslinkable functional group. Two epoxy group-containing vinyl monomers, namely glycidyl acrylate and glycidyl methacrylate, and one hydroxyl group-containing monomer, viz., N-methylolacrylamide, were used as comonomers. Conversions were limited to less than 10% by trial and error. The reaction medium for conducting copolymerization reactions and the method of isolating the copolymer from its monomers were arrived at after extensive screening of many solvents and nonsolvents in every case. The instantaneous copolymer composition versus composition of initial monomer mixture data was developed using wide variations in the composition of the initial monomer mixture for every pair of monomers copolymerized.

The reactivity ratios for six pairs of organotin vinyl monomers/ functional-group-containing vinyl monomers were determined by using the differential form of the copolymer equation based on the terminal model of binary copolymerization and the analytical YBR method of calculating reactivity ratios. The reactivity ratio data are summarized in Table 9, along with the estimates of errors in their determination, which were found to be small in every case.

The Q,e values were calculated for copolymerization of each of the organotin monomers using the Alfrey-Price equation, but it was not possible to assign Q,e values to either of the organotin monomers which were consistent for all of its copolymerizations. Therefore, the Q,e values were obtained by averaging all Q,e values calculated for the particular organotin monomer. These were Q = 0.852, e = 0.197 for tri-n-butyltin methacrylate; and Q = 0.235, e = 0.401 for tri-n-butylin

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TABLE 9. Reactivity Ratios for Copolymerization of Organotin Vinyl Monomers with Functional-Group-Containing Vinyl Monomers

Monomer M_1	Monomer M_2	Solvent	Precipitant	Temp. (°C)	$r_1 \pm \Delta r_1$	$r_2 \pm \Delta r_2$
Tri-n-butyltin acrylate	Glycidyl acrylate	Benzene	Methanol	75	0.295 ± 0.053	1.409 ± 0.103
	Glycidyl methacrylate	Benzene	Methanol	75	0.344 ± 0.201	4.290 ± 0.273
	N-Methylolacrylamide	Methanol	Water, then benzene[a]	65	0.977 ± 0.087	1.258 ± 0.038
Tri-n-butyltin methacrylate	Glycidyl acrylate	None	Methanol-water (80:20)	75	1.356 ± 0.157	0.367 ± 0.086
	Glycidyl methacrylate	None	Methanol-water (80:20)	75	0.754 ± 0.128	0.794 ± 0.135
	N-Methylolacrylamide	Methanol	Water, then benzene[a]	65	4.230 ± 0.658	0.381 ± 0.074

[a] The method of isolating the copolymer was first to add water to the reaction mixture, separate the precipitate and redissolve in methanol, and then add benzene to it to precipitate the copolymer.

acrylate. These values are comparable to Q,e values reported for other esters of acrylic and methacrylic acids in the literature.

The copolymerization of tri-n-butyltin methacrylate with glycidyl methacrylate was found to show azeotropic copolymerization at 46:54 mole ratio. For this particular copolymerization, the experimental results deviated significantly from the terminal model of binary copolymerization. The nature of deviation indicated that there was a significant alternating copolymerization, presumably through charge-transfer copolymerization, occurring in this case. It is indicated, thus, that the participation of organotin vinyl monomers in charge transfer copolymerizations should be further investigated. Such studies are underway in our laboratories.

Since the reactivity ratios indicate the distribution of the units of a particular monomer in the polymer chain, a suitable copolymer containing either blocks of organotin monomer units, blocks of vinyl monomer units containing functional-groups, alternating or random distributions of units of both monomers can be selected as desired. The presence of blocks of organotin monomer units, because of their elastomeric character, would lead to improved impact strength. Similarly, an improvement in tensile strength can be achieved by selecting the copolymer containing blocks of epoxy or hydroxyl group-containing vinyl monomer units. Finally, the copolymers containing an alternating or random distribution of the two comonomers might give the slowest leaching rate. The copolymer selected could subsequently be crosslinked with suitable crosslinking agents such as aliphatic or aromatic amines, Lewis acids or bases, epoxides, or diisocyanates to obtain thermoset organotin coatings with an optimal balance of mechanical and antifouling properties. Detailed results of these aspects of our investigation will be published separately.

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