SUMMARY

SUMMARY

In the present work three new vinyl monomers were prepared. Thus, p-acryloyloxybenzoic acid (ABA) was prepared by the reaction of p-hydroxybenzoic acid with acryloyl chloride. p-Acryloyloxy-tri-n-butyltin benzoate (ABTB) was prepared either by the reaction of acrylic acid with p-hydroxy-tri-n-butyltin benzoate in presence of N,N-dicyclohexylcarbodiimide (DCCI) as a condensing agent or by esterification of p-acryloyloxybenzoic acid with bis(tri-n-butyltin) oxide. Also, N-Methacryloyloxytetrabromophthalimide (NMTP) was prepared by either the reaction of methacrylic acid with N-hydroxytetrabromophthalimide in presence of DCCI or by the reaction of methacryloyl chloride with N-hydroxytetrabromophthalimide. The structure of these monomers was investigated by elemental analysis, IR, and NMR spectroscopy. Also, tri-n-butyltin acrylate or methacrylate monomers were prepared. The polymerization, copolymerization and terpolymerization reactions of these monomers with various vinyl monomers were investigated.

Binary copolymerization reactions of p-acryloyloxy-tri-n-butyltin benzoate (ABTB) with each of methyl acrylate (MA), ethyl acrylate (EA), n-butyl acrylate (BA), methyl methacrylate (MMA), styrene (ST) and acrylonitrile (AN) were studied. The monomer reactivity ratios for these six systems were calculated by both Fineman-Ross and Kelen-Tudos methods and were found to be :

system	Fineman-Ross method		Kelen-Tüdős method	
M_1 -M_2	r_1	r_2	r_1	r_2
ABTB-MA	0.122	1.062	0.080	1.046
ABTB-EA	0.049	1.575	0.039	1.585
ABTB-BA	0.016	2.147	0.019	2.076
ABTB-MMA	0.160	1.730	0.150	1.710
ABTB-ST	0.123	1.348	0.113	1.339
ABTB-AN	0.009	2.801	0.007	2.853

The results indicate that the monomer reactivity ratios of ABTB (r_1) for all systems studied are nearly equal to zero which indicate that the growing radical ending with ABTB unit prefers M_2 monomers than M_1 monomer in the propagation stage. The Q and e values for ABTB were calculated and found to be Q=0.45 and e=1.391. The structure of these copolymers was established by IR spectroscopy.

The binary copolymerization reactions of tri-n-butyltin acrylate (TBTA) with itaconic acid (IA), dimethyl itaconate (DMI), p-acryloyloxybenzoic acid (ABA) or N-methacryloyloxy-tetrabromophthalimide (NMTP) were studied. The monomer reactivity ratios for these four systems were calculated by Fineman-Ross and Kelen-Tudos methods and were found to be :

system	Fineman-Ross method		Kelen-Tüdős method	
M_1- M_2	r_1	r_2	r_1	r_2
TBTA-IA	1.088	0.011	1.086	0.070
TBTA-DMI	0.932	0.767	0.942	0.805
TBTA-ABA	1.000	0.360	1.014	0.399
TBTA-NMTP	0.691	0.902	0.689	0.896

It is clear that the monomer reactivity ratio values of TBTA (r_1) are greater than r_2 values for IA, DMI, and ABA, while in case of TBTA-NMTP system the r_1 value is lower than the r_2 value. Also, the r_1 and r_2 value of the copolymer systems TBTA-DMI and TBTA-NMTP are less than unity and should have azeotropic compositions at $F_1=f_1$ at the mole fractions of 0.77 and 0.25 respectively. The sequence distribution of the monomer units along the copolymer chains were calculated from the monomer reactivity ratios on the basis of terminal copolymerization model. The Q and e values for TBTA was found to be Q=0.313 and e=0.774 respectively. The structure of these copolymers was established by IR spectroscopy.

The binary copolymerization reactions of tri-n-butyltin methacrylate (TBTMA) with itaconic acid (IA), dimethyl itaconate (DMI), p-acryloyloxybenzoic acid (ABA) or N-methacryloyloxytetrabromophthalimide (NMTP) were studied The monomer reactivity ratios for these four systems were calculated by Fineman-Ross and Kelen-Tüdős methods and were found to be :

system	Fineman-Ross method		Kelen-Tüdős method	
$M_1 - M_2$	r_1	r_2	r_1	r_2
TBTMA-IA	2.272	0.073	2.157	0.006
TBTMA-DMI	1.223	0.829	1.242	0.869
TBTMA-ABA	2.190	0.820	2.207	0.861
TBTMA-NMTP	0.804	1.343	0.851	1.355

It is clear that the monomer reactivity ratio values of TBTMA (r_1) are greater than (r_2) values for IA, DMI and ABA, while in case of TBTMA-NMTP system the (r_1) value is lower than (r_2) value. The sequence distribution of the monomer unit along the copolymer chains were calculated from the monomer reactivity ratios on the basis of terminal copolymerization model. The Q and e values were calculated for TBTMA and were found to be Q=0.575 and e=1.300, respectvely. The structure of these copolymers was established by IR spectroscopy.

Azeotropy in binary and ternary copolymerization reactions of tri-n-butyltin acrylate or methacrylate with itaconic acid or dimethyl itaconate and acrylonitrile was investigated. The binary azeotropic composition of the system TBTA-DMI (F_1=77 mole %) was polymerized to several degrees covering a wide range of conversions and the results indicate that the experimental points are in good agreement with the theoretical composition . Four terpolymer systems involving tri-n-butyltin acrylate or methacrylate with itaconic acid, dimethyl itaconate and acrylonitrile were prepared. A computer program written in basic based on the equation proposed by Khan and Horowitz was used to facilitate the calculations of the ternary-polymer composition relatioship. The results obtained indicate that terpolymerization of both TBTA-IA-AN and TBTMA-IA-AN systems produced ternary azeotropic compositions at 39.00:26.10:10.90 and 51.70:10.50:37.80 mole % respectively. Also, compositions

obtained for TBTMA-DMI-AN system produced ternary azeotropic composition at 00.30:66.30:30.40 mole %. Selective feed compositions corresponding to unitary azeotropy for each system were polymerized to low conversions and the experimental terpolymer compositions are in good agreement with those obtained from theoritical calculations. Also, Selective comonomer compositions for each binary azeotropy in the terpolymer systems studied were polymerized and the results show that the experimental value are in good agreement with values obtained from theoritical calculations. The structure of the prepared terpolymers was investigated by IR spectroscopy.

Ternary copolymerization reactions of p-acryloyloxy-tri-n-butyltin benzoate with acrylonitrile and alkyl acrylates, methyl methacrylate or styrene was studied. The relation between monomer composition in the feed and instantaneous terpolymer composition is determined for each case and compositions obtained for all systems studied did not show any ternary azeotropic compositions. Selective feed compositions corresponding to unitary azeotropy for each system were polymerized to low conversion and the results illustrated show good agreement between the theoretical values and experimental ones. Also, selective comonomer compositions for each binary azeotropy for ABTB-BA-AN, ABTB-MMA-AN and ABTB-ST-AN terpolymer systems were polymerized to low conversions and the results indicate that for each system the experimental values are in good

agreement with values obtained from theoretical calculations. The structure of the prepared terpolymers was investigated by IR spectroscopy .

PUBLICATIONS FROM THE PRESENT WORK :

Parts of the present work have been subsequently published as follows:

1- Organotin Polymers - XIII - Binary Copolymerization Reactions of tri-n-butyltin Acrylate and Methacrylate With Itaconic Acid and Dimethyl Itaconate .
A.F. Shaaban, M.A. Salem, M.M. Azab and N.N. Messiha .
Acta Polymerica, 39, 654, (1988).

2- Organotin Polymers - XIV - Synthesis and Copolymerization Reactions of p-Acryloyloxy-tri-n-butyltin Benzoate With Some Vinyl Monomers .
Abd-El-Fattah Fadel Shaaban, Mohamed Morsy Azab and Nagi Naguib Messiha .
Die Angewandte Makromolekulare Chemie, 169, 59 (1989) .

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Organotin Polymers XIV [a]

Synthesis and Copolymerization Reactions of p-Acryloyloxy-tri-n-butyltin Benzoate with Some Vinyl Monomers

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SUMMARY:

p-Acryloyloxy-tri-n-butyltin benzoate (ABTB) was prepared by the reaction of p-hydroxy-tri-n-butyltin benzoate and acrylic acid in the presence of dicyclohexylcarbodiimide. The monomer reactivity ratios for the copolymerizations of ABTB (M_1) with methyl acrylate (M_2), ethyl acrylate (M_2), n-butyl acrylate (M_2), methyl methacrylate (M_2), styrene (M_2) and acrylonitrile (M_2) have been found to be r_1 = 0.080, r_2 = 1.046; r_1 = 0.039, r_2 = 1.585; r_1 = 0.019, r_2 = 2.076; r_1 = 0.150, r_2 = 1.710; r_1 = 0.113, r_2 = 1.339 and r_1 = 0.007, r_2 = 2.853, respectively. The Q and e values for the prepared organotin monomer were calculated. Copolymerization reactions were carried out in solution at 70 °C using 1 mol-% azobisisobutyronitrile. The structure of the ABTB monomer and the prepared copolymers was investigated by IR and ^{1}H-NMR spectroscopy.

ZUSAMMENFASSUNG:

p-Acryloyloxy-tri-n-butylzinnbenzoat (ABTB) wurde durch Reaktion von p-Hydroxy-tri-n-butylzinnbenzoat und Acrylsäure in Gegenwart von Dicyclohexylcarbodiimid hergestellt. Die Monomerreaktivitätsverhältnisse für die Copolymerisationen von ABTB (M_1) mit Methylacrylat (M_2), Ethylacrylat (M_2), n-Butylacrylat (M_2), Methylmethacrylat (M_2), Styrol (M_2) und Acrylnitril (M_2) wurden entsprechend zu r_1 = 0,080, r_2 = 1,046; r_1 = 0,039, r_2 = 1,585; r_1 = 0,019, r_2 = 2,076; r_1 = 0,150, r_2 = 1,710; r_1 = 0,113, r_2 = 1,339 und r_1 = 0,007, r_2 = 2,853 bestimmt. Die Q- und e-Werte für das zinnorganische Monomere wurden berechnet. Die Copolymerisationen wurden in Lösung bei 70 °C mit 1 mol-% Azobisisobutyronitril als Initiator durchgeführt. Die Struktur von ABTB und der hergestellten Copolymeren wurde durch IR-und ^{1}H-NMR-Spektroskopie untersucht.

[a] Part XIII cf. Acta Polym. **11** (1988) 645.

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1. Introduction

Acrylic polymers with pendent hydrolyzable organotin moieties have long been recognized as antifouling agents[1], wood preservatives[2] and more recently have demonstrated potential as mosquito larvicides[3].

Since properties of these organotin polymers are related to the distribution of monomer unites, it is of great interest to know the actual monomer reactivity ratios which control the sequence distribution. In our previous work[4-14] the copolymerizations of trialkyltin esters of acrylic, methacrylic, maleic and itaconic acids with various filmforming comonomers have been illustrated. The work is now extended to study copolymerizations of p-acryloyloxy-tri-n-butyltin benzoate with methyl acrylate, ethyl acrylate, n-butyl acrylate, methyl methacrylate, styrene, and acrylonitrile, in order to obtain suitable macromolecular chains, to which the organotin moieties could be attached at some distance from the main backbone.

2. Experimental

2.1 Materials

Tri-n-butyltin oxide (TBTO) was provided by M & T Chemical Inc., Rahway, New Jersey. Methyl acrylate (MA), ethyl acrylate (EA), n-butyl acrylate (BA), methyl methacrylate (MMA), styrene (ST), and acrylonitrile (AN) (E. Merck, Darmstadt, products) were purified by distillation under reduced pressure and the middle fractions retained for use.

2.2 Synthesis

p-Hydroxy-tri-n-butyltin benzoate (HBTB) was prepared through the esterification of p-hydroxybenzoic acid with TBTO. Thus, to a well stirred solution of 59.6 g (0.1 mol) of TBTO in 100 ml acetone was added 27.6 g (0.2 mol) of p-hydroxybenzoic acid for 30 min. at room temperature. The reaction mixture was left for 2 h and then evaporated to dryness. The residue was then recrystallized from light petroleum to yield 83.3 g (97.5%) of HBTB as colourless needles, melted at 68 °C and its tin content was found to be 27.74 % (calculated 27.87%).

p-Acryloyloxy-tri-n-butyltin benzoate (ABTB) was prepared by the reaction of acrylic acid with HBTB in presence of dicyclohexyl-carbodiimide (DCCl) as a condensing agent. Thus, a cooled solution of 20.6 g (0.1 mol) of DCCl in 30 ml methylene chloride was added dropwise to a cooled solution (5 – 10 °C) of 7.2 g (0.1 mol) of acrylic acid and 42.7 g (0.1 mol of HBTB in 70 ml methylene chloride with

stirring. Stirring was continued for 2 h at room temperature and the precipitated dicyclohexyl urea was removed by filtration. The filtrate after washing with dilute sodium bicarbonate solution was washed with water, dried over anhydrous sodium sulphate and then filtered. The resulting solution was evaporated under reduced pressure to give 42.2 g of ABTB monomer. The monomer produced was purified by washing several times with light petroleum and decantation of the supernatant liquid after cooling in the refrigerator. The excess of solvent was removed by distillation under reduced pressure. The monomer was found to melt at 30 – 32 °C and its tin content was found to be 24.63% (calculated 24.74%).

2.3 Polymerization Reaction

Polymerization of ABTB was carried out as follows: To a solution of 5 g (0.01 mol) ABTB monomer in 20 ml of dimethylformamide (DMF), 0.017 g (0.34 wt.-%) of azobisisobutyronitrile (AIBN) was added. After purging with nitrogen the solution was allowed to stand at 60 °C for 24 h. The resulting viscous polymer was obtained by reprecipitation from methanol, washed, dried, and weighed.

2.4 Copolymerization Reactions

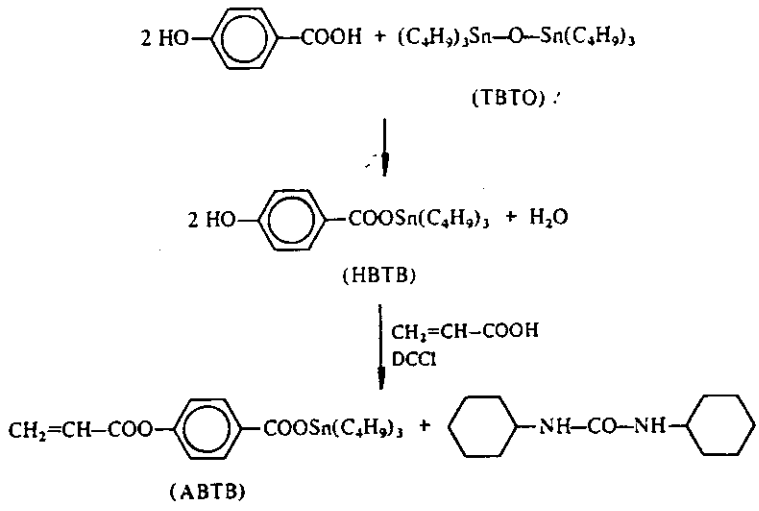
Binary copolymers from ABTB with MA, EA, BA, MMA, ST, and AN were obtained by solution polymerization in DMF (1.5 mol/l) at 70 °C, in the presence of 1 mol-% AIBN based on total monomer, according to the method previously described[6]. Overall conversions were limited to less than 10% in every case. 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 content of monomer, polymer and copolymers were determined by the method of Gilman and Rosenberg[15].

The infrared spectra were recorded on a Beckman 4220 spectrophotometer in the range of 4000 – 600 cm^{-1}. The proton magnetic resonance spectra (in $CDCl_3$ as a solvent and using TMS as a zero reference) were obtained at room temperature with a Varian EM-390 spectrometer operating at 90 MHz.

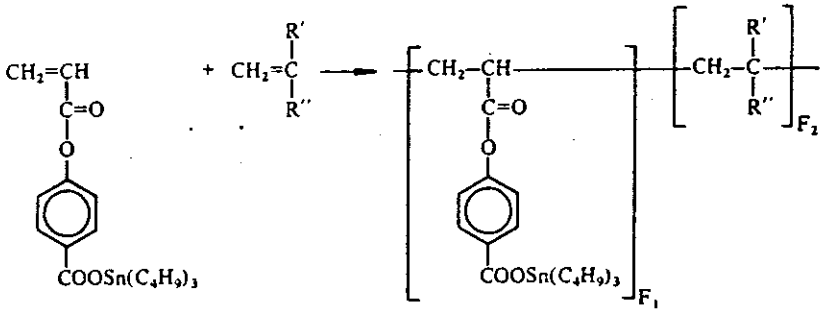
3. Results and Discussion

Organotin monomer ABTB described in this work has been prepared by the reaction of HBTB with acrylic acid in the presence of DCCI according to Scheme 1:



The prepared organotin monomer (ABTB) was found to polymerize slowly in presence of AIBN as radical initiator in DMF at 60 °C. The yield of polymer was 15% after 24 h. The structure of ABTB monomer and its polymer was investigated by IR and ^{1}H-NMR spectroscopy (Tab. 1 and 2, respectively).

In the present investigation the copolymerization reactions for ABTB with MA, EA, BA, MMA, ST, and AN were studied and the reactions can be represented by Scheme 2:



	R′	R″		R′	R″
MA	H	$COOCH_3$	MMA	CH_3	$COOCH_3$
EA	H	$COOC_2H_5$	ST	H	C_6H_5
BA	H	$COOC_4H_9$	AN	H	C≡N

Tab. 3. Analytical data for copolymerization reaction of ABTB with MA.

Feed composition M_1/M_2	Conversion (%)	Sn (%)	Copolymer composition M_1/M_2
0.6689	8.32	17.4765	0.4302
0.5375	7.52	16.4699	0.3561
0.4279	6.79	15.4786	0.2988
0.3335	6.99	13.9230	0.2301
0.2503	5.56	13.2033	0.2046
0.1763	8.39	11.3407	0.1513
0.1134	7.01	8.6319	0.0958
0.0495	7.42	5.0244	0.0456

plots for the six systems. It is clear from Tab. 4 that there is good agreement between the values of the reactivity ratios calculated by the two methods. The composition curves of the six binary copolymerization reactions studied are illustrated in Fig. 2. It is clear from Fig. 2 that the copolymers of ABTB-MA, ABTB-EA, ABTB-BA, ABTB-MMA, ABTB-ST, and ABTB-AN systems show lower content of F_1 than the monomer mixture. Tab. 4 shows that the monomer reactivity ratio values of ABTB (r_1) for all copolymerization reactions studied are nearly equal to zero, which indicates that the growing radical ending with ABTB unit rather prefers M_2 monomer than M_1 monomer in the propagation stage. The monomer reactivity ratio values of the vinyl monomers copolymerized with ABTB are greater than unity, which shows that the monomer sequence in these six copolymers consists of larger blocks of the comonomer units interrupted by single molecules of ABTB. Fig. 2 indicates that all systems studied do not give azeotropic copolymers.

The Q and e values for ABTB were calculated from the determined monomer reactivity ratios as well as the Q and e values of vinyl monomers[18] using the Alfrey-Price equations[19] as follows:

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

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

The average Q and e values for ABTB were Q = 0.450 and e = 1.391 which are in good agreement with the values reported in the literature[18] for the esters of acrylic acid.

Tab. 4. Monomer reactivity ratios for copolymerizations of ABTB with MA, EA, BA, MMA, ST, and AN.

M_1 – M_2	Fineman-Ross		Kelen-Tüdös		
	r_1	r_2	r_1	r_2	α
ABTB-MA	0.122 ± 0.065	1.062 ± 0.036	0.080 ± 0.003	1.046 ± 0.024	0.236
ABTB-EA	0.049 ± 0.048	1.575 ± 0.069	0.039 ± 0.001	1.585 ± 0.087	0.966
ABTB-BA	0.016 ± 0.016	2.147 ± 0.046	0.019 ± 0.001	2.076 ± 0.024	1.822
ABTB-MMA	0.160 ± 0.050	1.730 ± 0.050	0.150 ± 0.005	1.710 ± 0.006	0.357
ABTB-ST	0.123 ± 0.009	1.348 ± 0.011	0.113 ± 0.001	1.339 ± 0.009	0.737
ABTB-AN	0.009 ± 0.025	2.801 ± 0.098	0.007 ± 0.003	2.853 ± 0.072	3.066

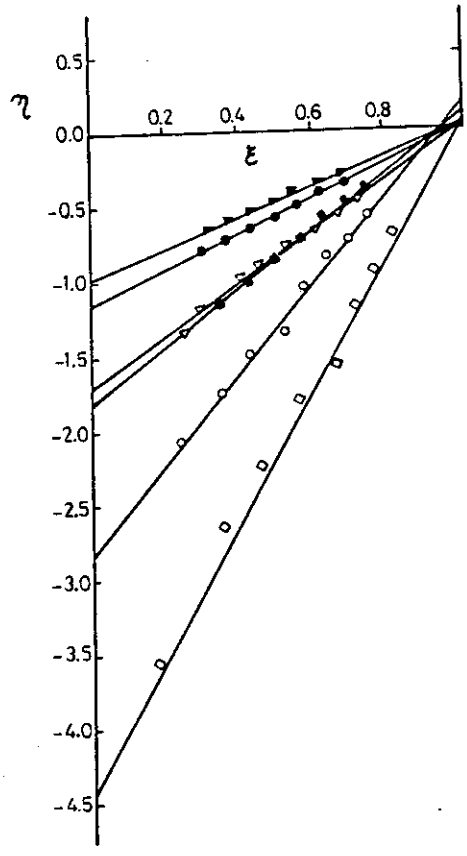


Fig. 1. Kelen-Tüdös plots for copolymerizations of ABTB with (□) MA, (△) EA, (●) BA, (○) MMA, (■) ST, and (▲) AN.
$\xi = \frac{a^2}{\alpha b + a^2}$ and $\eta = \frac{a(b-1)}{\alpha b + a^2}$ where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer, respectively, and
$\alpha = \frac{a_{min} \cdot a_{max}}{(b_{min} \cdot b_{max})^{1/2}}$
For α-values see Tab. 4.

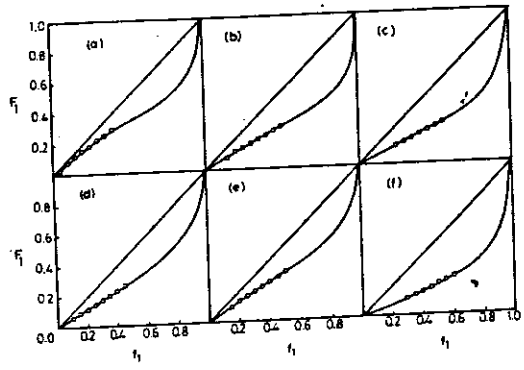


Fig. 2. Composition curves for copolymerizations of ABTB with (a) MA, (b) EA, (c) BA, (d) MMA, (e) ST, and (f) AN. Line represents calculated values and (○) represents experimental values; f_1 = molar fraction of M_1 in feed and F_1 = molar fraction of M_1 in copolymer.

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Organotin polymers.

XIII. Binary copolymerization reactions of tri-n-butyltin acrylate and methacrylate with itaconic acid and dimethyl itaconate

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The copolymerization reactions of tri-n-butyltin acrylate and methacrylate with itaconic acid and dimethyl itaconate, respectively, in solution with AIBN as initiator were studied. The composition of the copolymers was determined by tin analysis. The copolymerization parameters were calculated and discussed. The structure of the copolymers was investigated by infrared spectroscopy.

Organozinn-Polymere. XIII. Binäre Copolymerisation von Tri-n-butylzinn-acrylat und -methacrylat mit Itaconsäure und Dimethylitaconat

Die Copolymerisation von Tri-n-butylzinn-acrylat und -methacrylat mit Itaconsäure beziehungsweise Dimethylitaconat in Lösung bei Initiierung mit AIBN wurde untersucht. Die Zusammensetzung der Copolymere wurde aus dem Zinngehalt ermittelt. Die Copolymerisationsparameter wurden berechnet und diskutiert. Die Struktur der Copolymere wurde infrarotspektroskopisch bestimmt.

Оловоорганические полимеры. XIII. Бинарная сополимеризация три-н-оловобутилакрилата и метакрилата с итаконовой кислотой и диметилитаконатом

Исследовалась сополимеризация инициирования AIBN три-н-оловобутилакрилата и метакрилата с итаконовой кислотой или диметилитаконатом в растворе. Состав сополимеров определялся из содержания олова Параметры сополимеризации определялись и обсуждались. Структура сополимеров определялась ИК спектроскопией.

1. Introduction

Organotin polymers have long been used as pesticidal agents in antifouling formulations [1–3]. These controlled-release formulations were prepared either by addition copolymerization of organotin monomers with appropriate film forming comonomers or by esterification of pendent carboxyl groups on various linear polymers by bis(tri-n-butyltin) oxide. In our previous studies [4–8] the copolymerization parameters of tri-n-butyltin esters of acrylic and methacrylic acids with different vinyl monomers have been studied. These parameters are expected to be very useful in selecting a suitable copolymer with optimal physical properties. Much of these properties can be achieved by a knowledge of the monomer reactivity ratios which can be determined at the early stages of building up the macromolecules. The work is now extended to copolymerizations of tri-n-butyltin acrylate and methacrylate with itaconic acid and dimethyl itaconate.

2. Experimental

Tri-n-butyltin acrylate (BTA) and tri-n-butyltin methacrylate (BTMA) were prepared according to the method of CUMMINS and DUNN [9] by the reaction of bis(tri-n-butyltin) oxide with acrylic or methacrylic acids, respectively. Itaconic acid (IA) and dimethyl itaconate (DMI) were obtained from E. Merck, Darmstadt. Azobisisobutyronitrile (AIBN) was crystallized from alcohol, m.p. 102 °C.

Organotin copolymers were obtained by solution polymerization in toluene (3 mol/l) at 70 °C with 1 mole-% AIBN according to the method previously described [6]. The copolymers were purified by reprecipitation from 90% methanol, washed, dried and weighed. Tin contents of the copolymers were determined by the method of GILMAN and ROSENBERG [10].

3. Results and discussion

In the present investigation the copolymerization parameters for the copolymerization reactions of BTA or BTMA with IA and DMI were determined. Table 1 shows the analytical data for the copolymerization reaction of BTMA with DMI as an example. The monomer reactivity

Table 1. Analytical data for copolymerization of BTMA with DMI

Feed composition (M_1/M_2)	Conversion %	Sn %	Copolymer composition (M_1/M_2)
1.4999	7.11	25.66	1.7800
1.8571	6.96	26.80	2.2888
2.3333	7.35	27.52	2.7521
2.9992	8.04	28.57	3.7992
4.0000	6.79	29.25	4.9556
5.6669	5.97	30.17	6.8634

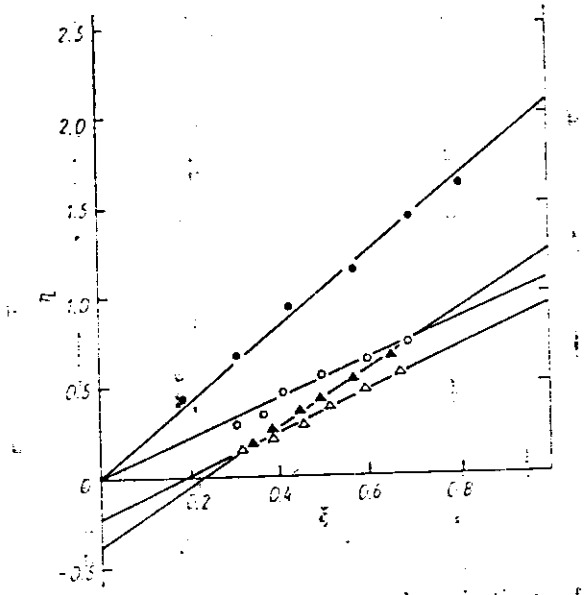

Fig. 1. KELEN-TÜDÖS plots for copolymerizations of (○) BTA-IA, (△) BTA-DMI, (●) BTMA-IA, and (▲) BTMA–DMI.

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

where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer, respectively, and

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

ratios (r_1 and r_2) for each system were deduced from the analytical data by both the FINEMAN-ROSS [11] and KELEN-TÜDŐS [12] methods, and the standard deviations of the results were calculated by regression analysis as illustrated in Table 2. Figure 1 shows the KELEN-TÜDŐS plots for the copolymerization reactions of BTA or BTMA with IA and DMI.

The monomer reactivity ratios in Table 2 indicate that the copolymerizations of BTA and BTMA with IA shows a tendency towards the formation of a block copolymer, while the copolymerizations of BTA or BTMA with DMI should have random distribution of the monomer units in the copolymer chain and the tendency towards alternation increases in the BTA-DMI system.

The sequence distributions of the monomer units along the copolymer chains were calculated from the monomer reactivity ratios on the basis of terminal copolymerization model [12]. The variation in the sequence distribution of the triad fractions (f_{111}, f_{112} and f_{212}) with feed composition are represented in Figure 2. It is clear that the triad fractions f_{111} increase with increasing of f_1 while triad fractions f_{212} decrease with increasing of f_1. Triad fractions f_{122} have maximum values at f_1 equal to 0.50, 0.50 0.30, and 0.45 for BTA-IA, BTA-DMI, BTMA-IA, and BTMA-DMI, respectively.

From Table 2, it is clear that the monomer reactivity ratios r_1 and r_2 for the BTA-DMI system are both less than one, and the copolymerization reaction of this system should have azeotropic character. The composition curves (Figure 3) for the copolymerization of BTA with DMI cross the line representing $F_1 = f_1$ at mole fraction 0.77. This point of intersection corresponds to the azeotropic composition yielding a homogeneous copolymer regardless of conversion. However, the copolymerization of BTA-IA, BTMA-IA, and BTMA-DMI gave no azeotropic copolymers.

The prepared copolymers of BTA or BTMA with IA

Table 2. Monomer reactivity ratios for copolymerizations of BTA and BTMA with IA and DMI

M_1-M_2	FINEMAN-ROSS Method		KELEN-TÜDŐS Method		r_1r_2	α
	r_1	r_2	r_1	r_2		
BTA—IA	1.088 ± 0.044	0.011 ± 0.109	1.086 ± 0.113	0.070 ± 0.121	0.076	2.038
BTA—DMI	0.932 ± 0.040	0.767 ± 0.181	0.942 ± 0.072	0.805 ± 0.166	0.758	3.661
BTMA—IA	2.272 ± 0.080	0.073 ± 0.090	2.157 ± 0.161	0.006 ± 0.046	0.013	0.524
BTMA—DMI	1.223 ± 0.036	0.829 ± 0.101	1.242 ± 0.064	0.869 ± 0.099	1.079	2.432

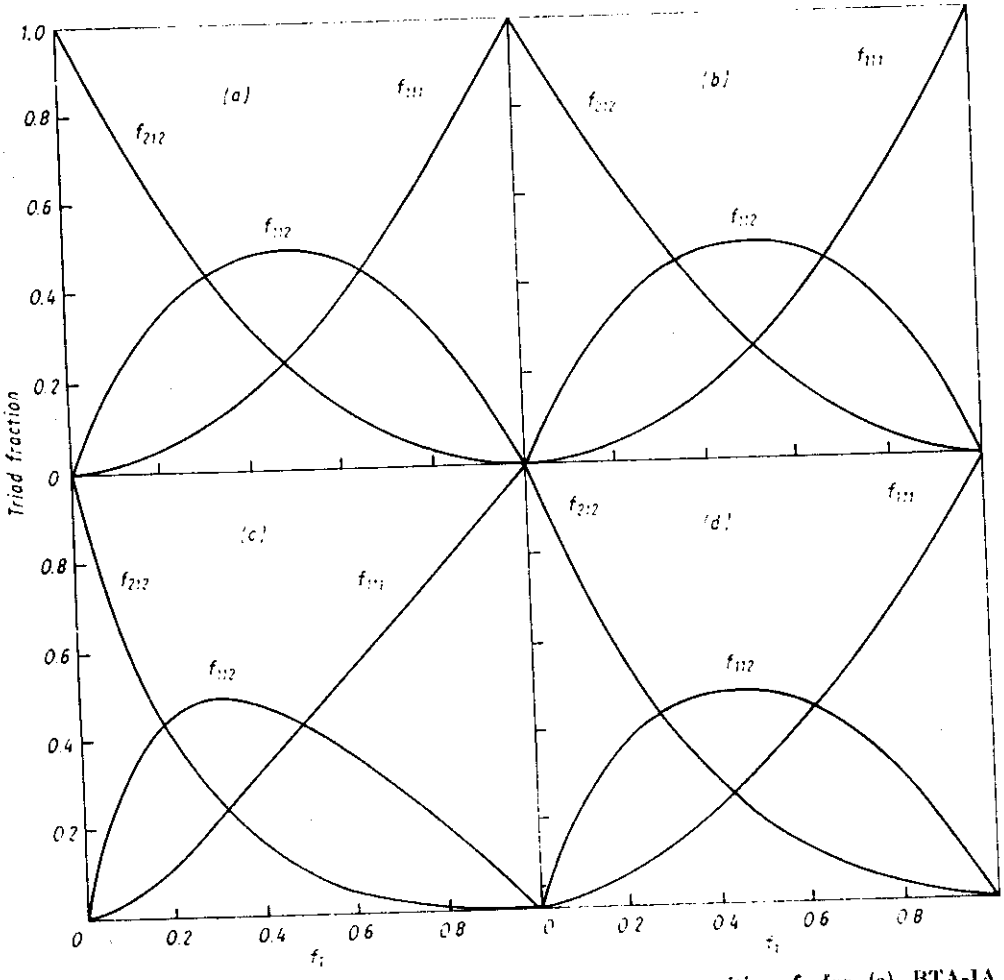

Fig. 2. Dependence of triad fractions (f_{111}, f_{112} and f_{212}) on comonomer composition f_1 for (a) BTA-IA, (b) BTA-DMI, (c) BTMA-IA, and (d) BTMA-DMI

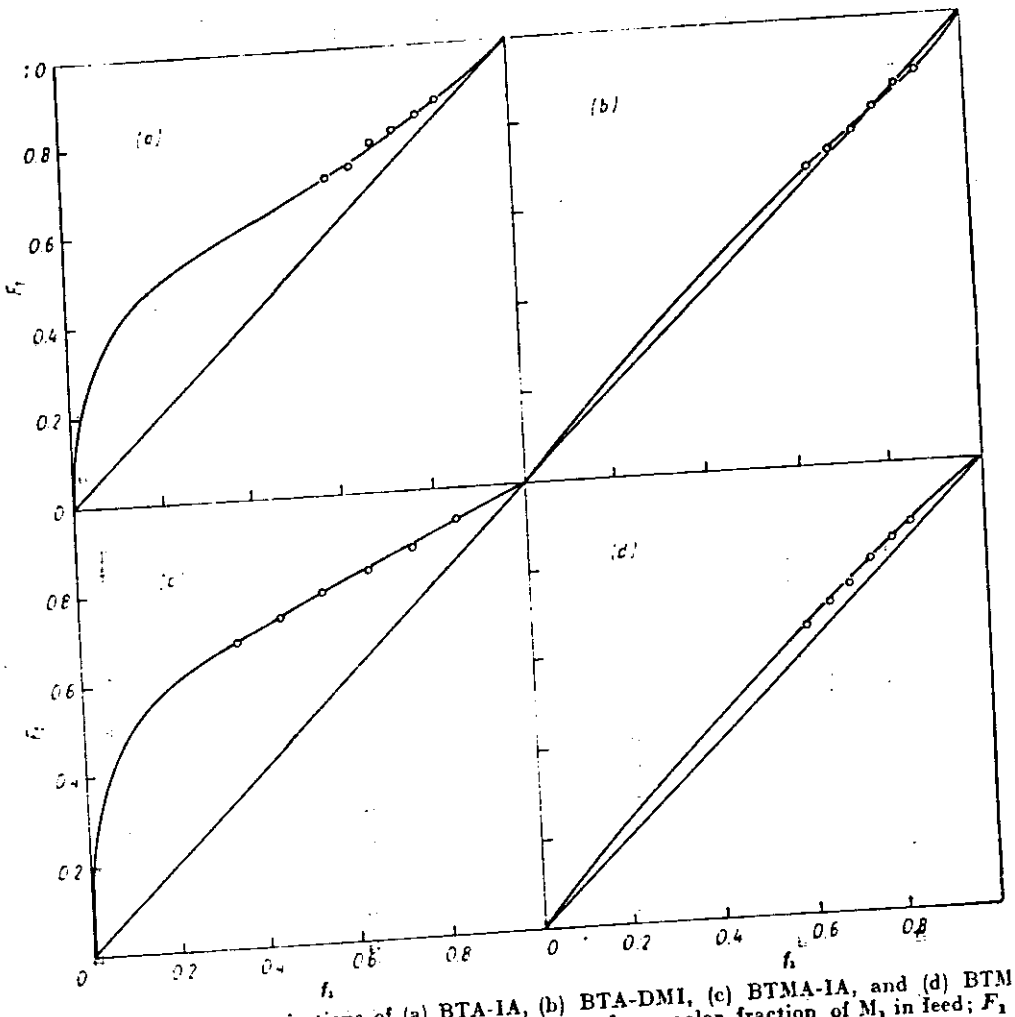

Fig. 3. Composition curves for copolymerizations of (a) BTA-IA, (b) BTA-DMI, (c) BTMA-IA, and (d) BTMA-DMI. Line represents calculated values and (○) represent experimental values. f_1 — molar fraction of M_1 in feed; F_1 — molar fraction of M_1 in copolymer

and DMI are solid and clear products, soluble in most organic solvents and suitable for film formation. The IR spectrum of the BTA-DMI copolymer shows two absorption bands, one characteristic of the carboxylate group of the tetra-coordinated tin atom [9] at 1640 cm^{-1} and the other at 1730 cm^{-1} due to the ν(C=O) of the ester group.

The Q and e values were calculated from the monomer reactivity ratios by the ALFREY-PRICE equations [13]:

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

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

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 [14] from earlier copolymerization data. Thus, the Q and e values for BTA and BTMA were obtained by using the monomer reactivity ratios determined for the systems BTA-DMI and BTMA-DMI (Table 2) and using the Q and e values for the itaconic acid and dimethyl itaconate [15, 16]. The product $r_1 r_2$ for BTMA-DMI was found to be > 1 and was thus set equal to 1 so that equation (1) could be solved [17]. The Q and e values for BTA and BTMA were calculated (Table 3) and have been found to be comparable with those reported in the literature [18]. The values of the product $r_1 r_2$ for the systems BTA-IA and BTMA-IA were approximately zero, and thus equations (1) and (2) resulted in abnormal Q and e values.

Table 3. Calculated Q and e values for BTA and BTMA

Monomer	Q	e
BTA	0.313	0.774
BTMA	0.575	1.300

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