Radical Copolymerization of 3-Tri-n-Butylstannylstyrene with Several Vinyl Monomers

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Synopsis

The free radical homopolymerization and copolymerization of 3-tri-n-butylstannylstyrene (3-BTS) with styrene (ST), ethyl acrylate (EA), methyl methacrylate (MMA), vinyl acetate (VA), and acrylonitrile (AN) were carried out using 2,2'-azobisisobutyronitrile (AIBN) at 60°C. It was found that the yield of conversion to poly(3-BTS) increased with the molar ratio of initiator to monomer as well as with polymerization time. The conversion at equilibrium after 50 h was about 40%. The compositions of copolymer samples were determined from elemental analyses. Monomer reactivity ratio and Q–e values were calculated. The copolymers of 3-BTS-MMA and 3-BTS-AN were found to be alternating. The copolymers of 3-BTS with MMA, EA and AN were not soluble in any of a large number of organic solvents tested. The insolubility is believed to be due to formation of intermolecular coordination among the tributylstannyl moiety and the carbonyl or cyano groups of the polymer. These copolymers, however, were "soluble" in trihaloacetic acid, but this solubility was due to a cleavage of the trialkyltin moiety from the phenyl groups. The glass temperatures, T_g, and melting temperatures T_m, of the various polymers were also studied.

INTRODUCTION

Polymerization of several styrene derivatives with organotin groups were previously reported by our group.[1] It was found that the inhibition effect of the tin moiety on polymerization depended considerably upon the position of the tri-alkyltin moiety on the phenyl group because of conjugation as well as polar and steric effects between the organotin and vinyl groups. 3-Tri-n-butylstannylstyrene (3-BTS) showed good copolymerizability with methyl methacrylate under radical polymerization conditions.

The aim of this work was to study the copolymerizability of 3-BTS with styrene (ST), ethyl acrylate (EA), methyl methacrylate (MMA), vinyl acetate (VA), and acrylonitrile (AN). A further goal was to determine monomer reactivity ratios, monomer composition, reaction mechanism, and thermal properties of the copolymers.

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EXPERIMENTAL

Materials

2,2'-Azobisisobutyronitrile (AIBN) was used without purification. To remove inhibitors from the monomers they were washed repeatedly with aqueous 5% NaOH and with saturated aqueous $CaCl_2$. After drying over anhydrous $MgSO_4$, the monomers were distilled under reduced pressure and an atmosphere of nitrogen. Just before use, they were always redistilled.

3-Tri-*n*-butylstannylstyrene (3-BTS) was prepared with some modification as described earlier.[1,2]

Method A

A suspension of 0.57 g (0.023 mol) of magnesium turnings in 8 mL THF was gently refluxed in a three-necked flask equipped with two dropping funnels, and a reflux condenser. To this mixture several drops of 1,2-dibromoethane were added to activate the metal. A solution of 3.3 g (0.018 mol) of 3-bromostyrene in 50 mL THF was then added dropwise to the suspension of activated magnesium metal simultaneously with 6.2 g (0.016 mol) of tri-*n*-butylstannyl chloride in 40 mL THF by using two dropping funnels. The remaining 1 g (0.005 mol) of the 1,2-dibromoethane was added as needed to maintain a smooth exothermic reaction. After the magnesium was consumed (about 60–90 min) the reaction mixture was stirred at 50°C for about 30 min, then allowed to cool to room temperature, when it was decomposed by adding 150 mL of a saturated ammonium chloride solution. The organic layer was separated, the aqueous layer was extracted twice with 70 mL portions of benzene, and the combined organic layers were dried over anhydrous $MgSO_4$. After distilling off the solvents under vacuum the remaining liquid was purified by column chromatography using benzene as elutant to give 5.1 g (81% yield) of product. For final purification it was distilled under vacuum.

Method B

To a three-necked flask under argon at −78°C containing 3.3 g (0.018 mol) of 3-bromostyrene in 30 mL dry tetrahydrofuran was gradually added 9.1 mL (0.018 mol) of 1.97*N* *n*-butyllithium in hexane solution. After stirring for 15 min 5.33 g (0.016 mol) of tri-*n*-butylstannyl chloride in 30 mL, THF was added gradually. After the addition was completed the mixture was stirred for 15 min and then allowed to warm gradually to room temperature. After 30 min 150 mL of saturated ammonium chloride solution was poured into the mixture to terminate the reaction and to dissolve the Li-salt. The organic layer was separated and worked-up as in method A, giving 3.2 g (50.7%) of product before distillation; bp 125–135°C/0.1 mm Hg. IR (neat), cm^{-1}: 2900, 1625. ^{1}H-NMR ($CDCl_3$) δ: 0.43–2.12 (m, 27H, *n*-butyl groups; δ, 5.1–5.9 (dd, 2H, $CH_2=$, $J = 18, 10$ Hz); δ, 6.76 (dd, $=CH=$, 1H, $J = 18, 11$ Hz); δ, 7.4 (m, 4H, aromatic H).

ANAL. Calcd for $C_{20}H_{34}Sn$ (MW 393.19): C, 61.09; H, 8.71. Found: C, 61.18; H, 8.64.

The yields obtained by either method vary because of loss of product by polymerization during distillation. Attempts to carry out the distillation in the presence of hydroquinone did not prevent this partial loss.

Preparation of Polymers

Free radical induced homo- and copolymerizations were carried out under an atmosphere of nitrogen in sealed glass ampoules. The appropriate monomer and AIBN were simultaneously charged into an ampoule, which was then sealed, cooled below 0°C and placed in an oil bath at 60°C during the periods of polymerization. After polymerization the vessel was cooled by immersing it into an ice bath for 0.5 h. The polymers produced were precipitated by pouring the solutions into an excess of methanol. They were filtered, vacuum dried at 30°C, powdered, dissolved in benzene, and reprecipitated by methanol to remove unreacted monomers and oligomers. The isolations and extractions of copolymers were carried out by sequential extractions.

Characterization of Polymers

The content of C, H, and N in each polymer was determined using a CHN-Analyzer, Model 185 B, Hewlett-Packard. The tin content was analyzed by inductively coupled, plasma atomic emission spectroscopy employing a LAPTAN-3000 instrument.

IR spectra were obtained on either a Perkin-Elmer Model 599 or a Nicolet MX-5 FT IR spectrometer. Polymer films for spectroscopic investigations were prepared by casting them from a benzene solution. ^{1}H-NMR spectra were recorded on a Varian T-60A NMR spectrometer.

The glass transition temperature, T_g, and melting point, T_m, of each polymer were determined from DSC diagrams recorded on a DuPont 990 Thermal Analyzer, using a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Homopolymerization of 3-Tri-n-Butylstannylstyrene

Radical polymerizations of 3-BTS with AIBN were carried out using various concentrations of monomer and initiator at 60°C. Poly(3-BTS), which is a colorless, amorphous, and somewhat tacky solid, is slightly soluble in solvents such as benzene and toluene, but insoluble in cyclohexane, methyl ethyl ketone, and dioxane.

The relationships among the conversion, polymerization time and the ratio of concentration of initiator to monomer are shown in Table I. The conversion reached equilibrium after 60 h with a yield of polymer of about 41% by weight. The rate of polymerization of 3-BTS is slower than that of styrene, probably due to steric hindrance from the tri-n-butylstannyl substituent.

It is assumed that the observed decrease of solubility with increase in polymerization time was caused by a complexation between the tin atom of the side chain and the phenyl ring of the styrene moiety. The increase in conversion yield with increase in AIBN concentration appears to result from the non-radical-induced decomposition[3] of 3-BTS by AIBN and the ease of forming a complex as depicted in Scheme 1.

Characteristic IR absorption bands of poly(3-BTS) appeared at 1605, 1570, 1475, and 1430 cm^{-1}. They are due to the in-plane stretching vibrations of phenyl rings and the deformation modes of $-CH_2-$ groups (Fig. 1). Bands

TABLE I
Copolymerization of 3-BTS with ST, EA, MMA, VA, and AN at 60°C

Sample	M_2 [a] (mmol)	$[M_1]/[M_2]$ [b]	AIBN (mol %)	Polymerization time (h)	Conversion (wt %)	Elemental analysis (wt %)				F [c]	f [d]	T_g (°C)	T_m (°C)
						C	H	N	Sn				
Poly(3-BTS)	—	2.5	0.6	24	13.0	49.8	4.78	—	42.91	—	—	82	322 345 314
Copoly(3-BTS–ST)	2.52	1.0	0.5	12	36.0	70.6	8.85	—	15.20	0.27	5.55	66	330
Copoly(3-BTS–EA)	2.59	1.0	0.6	5	19.6	63.0	9.01	—	0.99	0.01	1.04	95	330
Copoly(3-BTS–MMA)	2.57	1.0	0.5	5	12.1	62.8	8.90	—	22.3	0.63	1.07	90	345 325
Copoly(3-BTS–VA)	2.52	1.0	0.5	12	1.6	61.7	9.06	—	17.0	0.15	1.05	72	355 322
Copoly(3-BTS–AN)	0.14	0.9	0.5	5	38.3	52.5	6.67	4.36	24.9	0.68	10.35	—	350 —

[a] M_2 = ST, EA, MMA, VA, and AN.
[b] The ratio of initial concentrations for M_1 and M_2, M_1 = 3-BTS.
[c] Molar ratio of compositions in copolymer.
[d] The molar ratio of feed quantities.

at 1355, 1300, and 1190 cm^{-1} are due to wagging and twisting modes of —CH$_2$— and CH— groups in the vinyl group and those at 880, 780, and 695 cm^{-1} are assigned to the out-of-plane deformation vibration of the hydrogen atom at the meta position of the disubstituted phenyl ring. The band at 610 cm^{-1} is due to the stretching vibration of the —Sn—CH$_2$— bond of the tri-n-butylstannyl group and finally the one at 440 cm^{-1} is attributed to the stretching vibration of —Sn—C— bond of the phenyl-tin linkage.

Absorption bands in the region between 450 and 530 cm^{-1}, which are typical of the normal position for the —Sn—CH$_2$— bond,[4] appeared at 610 cm^{-1} as symmetric stretching vibrations.

Symmetrical deformation vibrations of the —CH$_2$— group which are closest to the tin atom are related to changes of H—C—H angles and appeared at 1190 cm^{-1} as a result of the complex formation.[5] Bands at 1635, 1415, and 910 cm^{-1} corresponding to stretching and deformation vibrations of the vinyl group in the monomer were not observed in poly(3-BTS).

The ^{1}H-NMR spectrum of poly(3-BTS) also is shown in Figure 1. The resonances observed at $\delta = 7.30$–6.10 ppm are due to protons of the phenyl ring and those at $\delta = 2.60$–0.60 ppm are due to protons of the —CH$_2$—CH— group of the backbone and of the three n-butyl groups. Peaks at $\delta = 5.1$–5.9 and $\delta = 6.76$ ppm are due to protons of the vinyl group of the monomer. They are not observed in the polymer. The resonances of poly(3-BTS) at $\delta = 7.30$–6.10 ppm indicate that the polymer obtained had an atactic configuration[6] because of inter- and intramolecular complexation, as shown in Scheme 1.

It is assumed that radicals of the growing chains attack 3-BTS at the less hindered side. Cross-linking by complexation would depend on polymerization conditions and the chain length of the polymer.

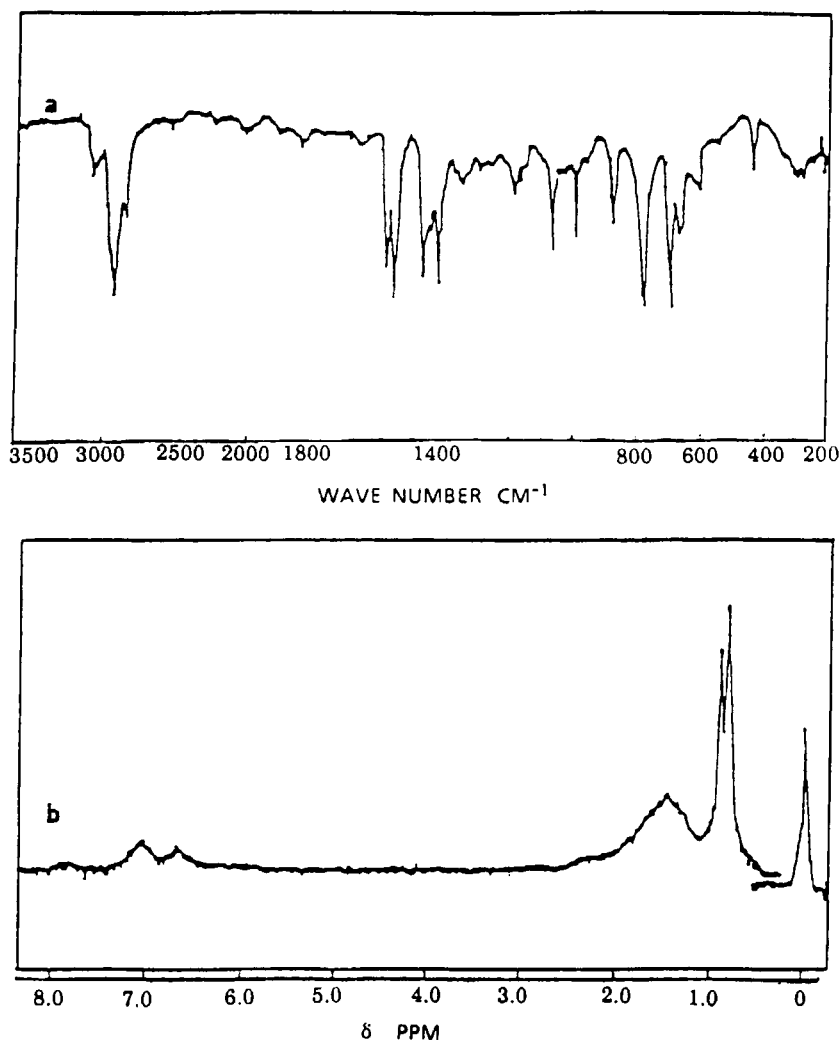$$R = n\text{-}C_4H_9$$
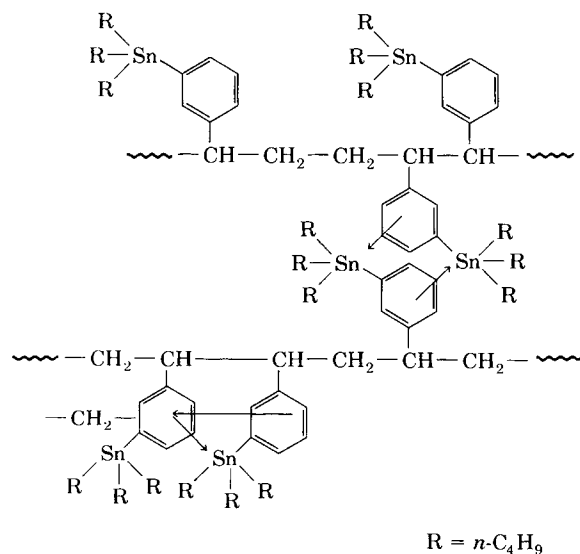
Scheme 1.

Fig. 1.   IR spectrum (a, film) and ^{1}H-NMR spectrum (b, CDCl$_3$) of poly(3-BTS).

Copolymerization of 3-Tri-*n*-Butylstannylstyrene with Several Vinyl Monomers

The radical copolymerizations of 3-BTS with ST, EA, NMA, VA, and AN gave solids which were colorless, amorphous, somewhat tacky, and rubberlike in appearance.

Copolymers 3-BTS–MMA, 3-BTS–EA, and 3-BTS–AN were insoluble in a large number of solvents. Solvents which seem to dissolve the copolymers, however, actually did this by cleaving the — Sn — C — aromatic bonds.

Copolymerization conditions and the obtained results are listed in Table I. The copolymer compositions were calculated from the results of the elemental analysis of C, H, N, and Sn and the mass balance.
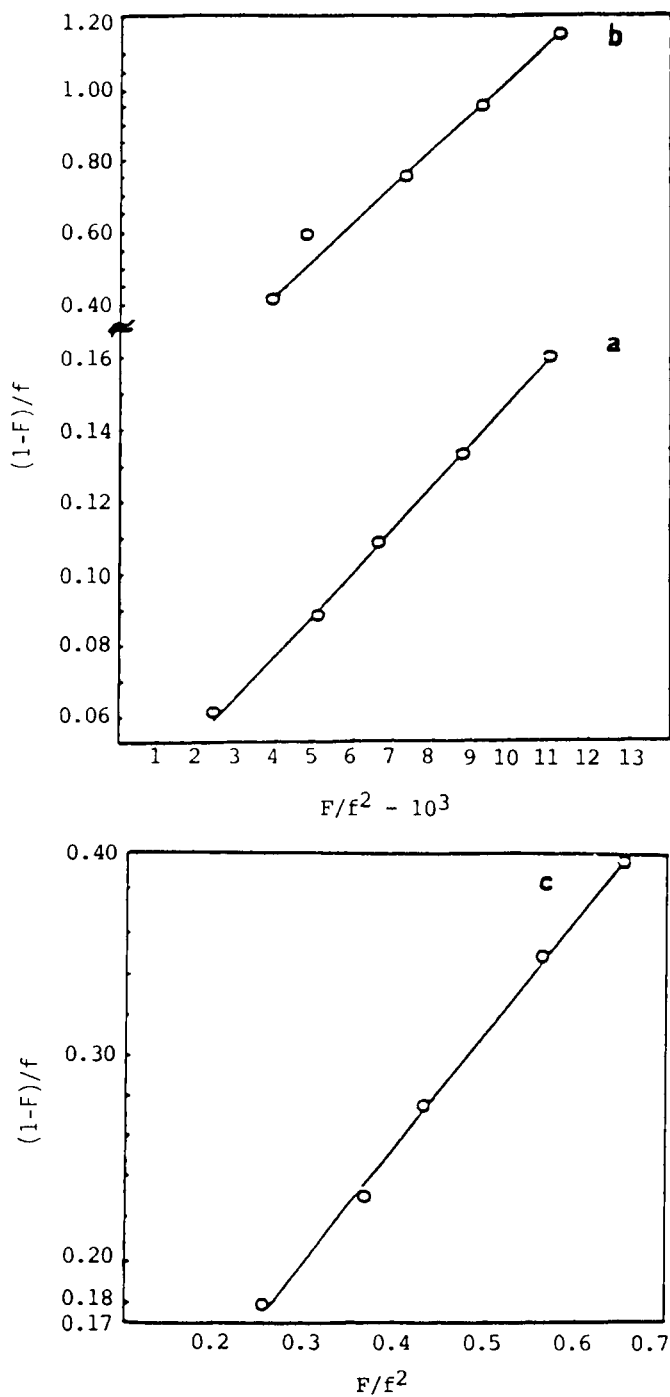
Fig. 2. $(1 - F)/f$ vs. F/f^2 for copolymerization reactivity ratios in poly(3-BTS–ST) (a), –EA (b), –MMA (c), –AN (d), and –VA (e).
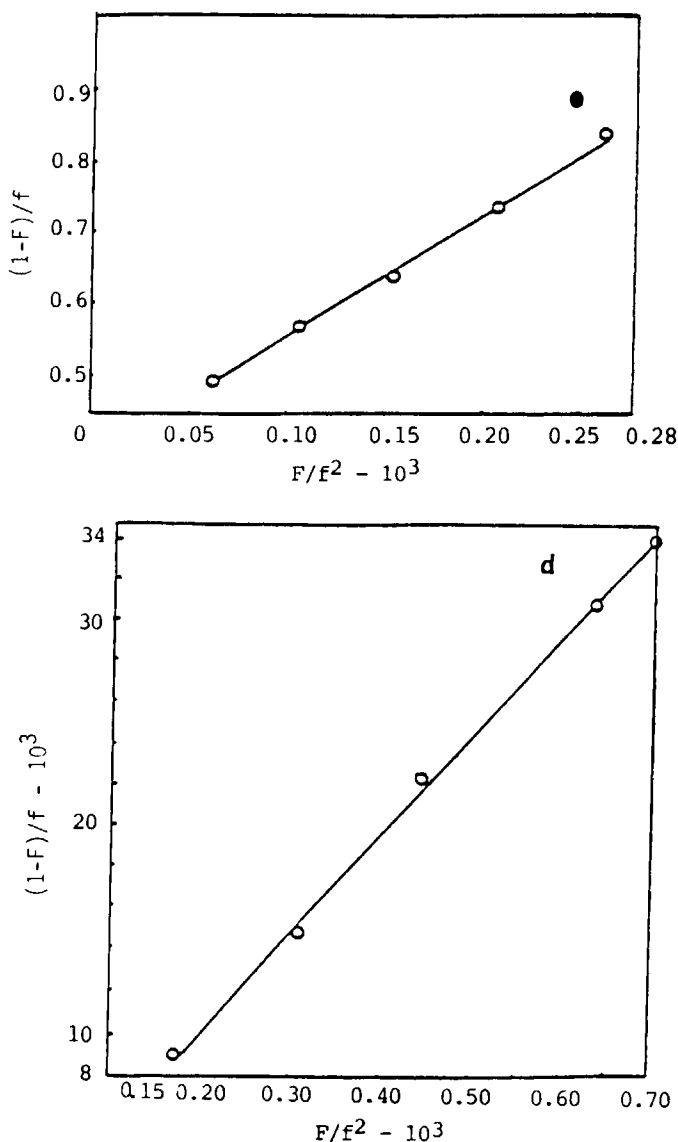
Fig. 2.   (Continued from the previous page.)

Monomer reactivity ratios r_1 and r_2 were evaluated by eq. (1)[7,8]

$$(1 - F)/f = r_2(F/f^2) - r_1 \qquad (1)$$

where F represents the molar ratio of two monomers in the polymer formed when the corresponding ratio of unreacted monomers is f. Relationships between $(1 - F)/f$ and F/f^2 are shown in Figure 2. $Q-e$ values as proposed by Alfrey and Price[8] were calculated from r_1 and r_2, and are shown in Table II.

TABLE II

Monomer Reactivity Ratio r_1, r_2 and Q–e Values[a] for Copolymers of 3-BTS Prepared at 60°C Using AIBN

M_1	M_2	r_1	r_2	$r_1 r_2$	e_1	Q_1
3-BTS	ST	0.03	18.5	0.56	−1.57	0.10
	EA	0.01	10.4	1.04	—	—
	MMA	0.03	0.69	0.02	−1.56	0.47
	VA	0.38	5.33	2.03	—	—
	AN	0.4×10^{-4}	4.88	2.00×10^{-4}	−1.72	0.0

[a]ST: $e = -0.80$, $Q = 1.00$; EA: $e = 0.22$, $Q = 0.52$; MMA: $e = 0.40$, $Q = 0.74$; VA: $e = -0.22$, $Q = 0.026$; AN: $e = 1.20$, $Q = 0.60$.

As the data of Tables I and II reveal, the molar quantities of 3-BTS in the copolymer decreased in the order, AN > NMA > ST > VA > EA. The values of r_1 and r_2 were observed to increase in the order, AN < NMA < ST < EA < VA.

As mentioned above, it is clear that 3-BTS has good copolymerizability with MMA and AN, but not as good with EA and VA under the described conditions.

3-BTS redicals at the end of the growing chains prefer to attack vinyl monomers M_2 because of steric and polar effects from the tri-n-butylstannyl group. Another contributing factor is the resonance stabilization of M_2, which was found to increase in the following order, VA < MMA < ST < EA < AN. However, M_2 radicals prefer to attack themselves because of steric and polar effects of the tri-n-butylstannyl group in 3-BTS.

The values of monomer composition as molar ratio of M_1 to M_2 in copolymer 3-BTS–AN, 3-BTS–MMA, and 3-BTS–ST were 0.68, 0.63, and 0.27, respectively.

The e_1 values[9] characterizing the polarity of 3-BTS (Table II) were more negative than those of styrene (-0.80), 4-methoxystyrene (-1.11), 3-methyl-styrene (-0.78), and 3-chlorobenzene (-3.6).

It can be assumed that the value of e_1 for 3-BTS, being more negative than that of styrene, makes the copolymer with M_2 more nearly alternating because of the electron-withdrawing group in M_2 and the polarity effect of the organotin group of 3-BTS through a spatial effect. Larger negative e_1 values increase the acceptor property of the tri-n-butylstannyl group when M_2 is incorporated with 3-BTS.

The Q_1 values[9] characterizing the resonance term (Table II) were less than those of styrene (1.00), 4-methoxystyrene (1.36), 3-methoxystyrene (0.11), and 3-chlorobenzene (1.03). From the Q_1 values of poly(3-BTS–ST), poly(3-BTS–MMA), and poly(3-BTS–AN), it follows that the stability of resonance contribution in 3-BTS is decreased by the steric effect of the tri-n-butylstan-nyl group. Thus, it becomes clear that vinyl monomers with electron with-drawing groups by a resonance or an inductive effect would have good copolymerizability with 3-BTS. The values of e_1 and Q_1 of 3-BTS were -1.72, -1.56, and 0.47, respectively.

The IR spectra of the copolymers of 3-BTS with the M_2 vinyl monomers are shown in Figures 3–5. Their characteristic IR data are summarized in
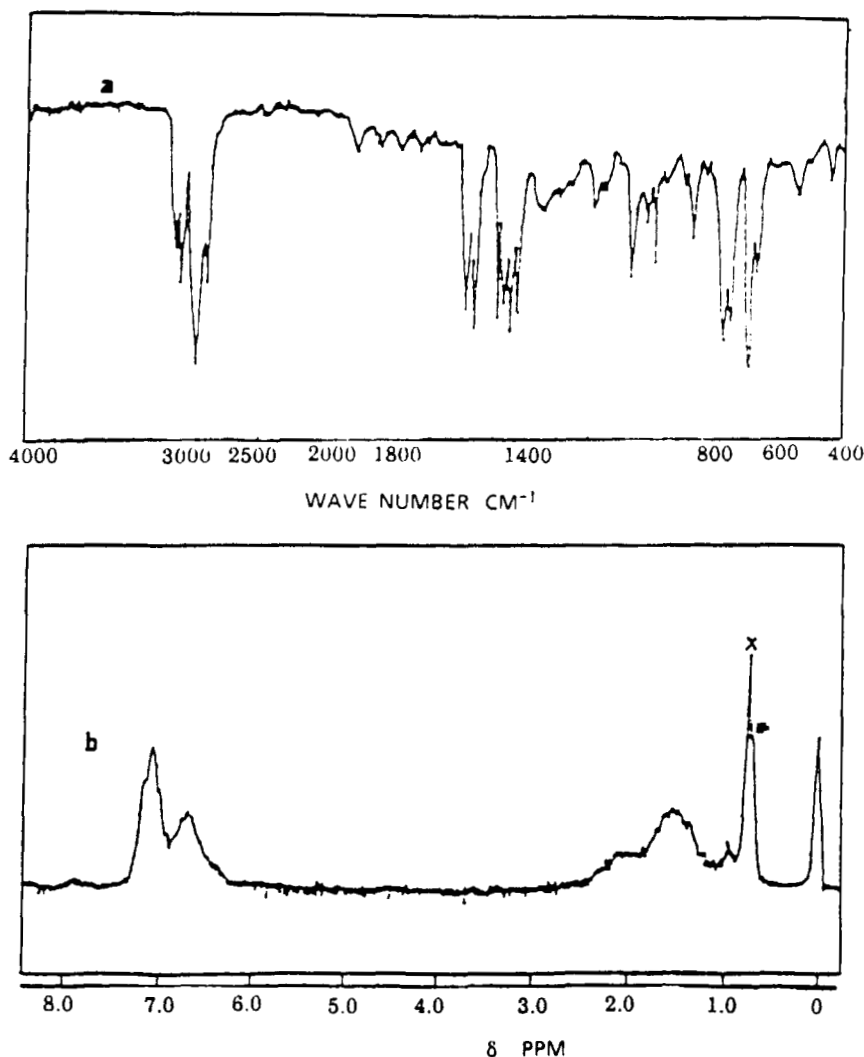
Fig. 3.   IR spectrum (a, film) and ^{1}H-NMR spectrum (b, C_6D_6) of poly(3-BTS-ST).

Table III. IR spectra for copolymers 3-BTS–EA, 3-BTS–MMA, and 3-BTS–AN could not be obtained as a film or as a KBr disc because of their insolubility and rubber-like properties. Thus, these copolymers were swollen in benzene before preparation of KBr discs, and measured using a FT–IR spectrophotometer.

It can be seen from Table III that the IR absorption frequencies of the —Sn—CH$_2$— group in the copolymers are shifted to a higher region, by 110–160 cm^{-1}, from the normal positions.[4] The stretching vibrational absorption due to —Sn—CH$_2$— occurred at 560 cm^{-1} because of lower tin contents and less restriction of the rotations of n-butyl groups in copoly(3-BTS–ST) than in poly(3-BTS).

The shift to higher frequencies observed in copolymers 3-BTS–EA, 3-BTS–MMA, and 3-BTS–AN is assumed to be related to the effects of
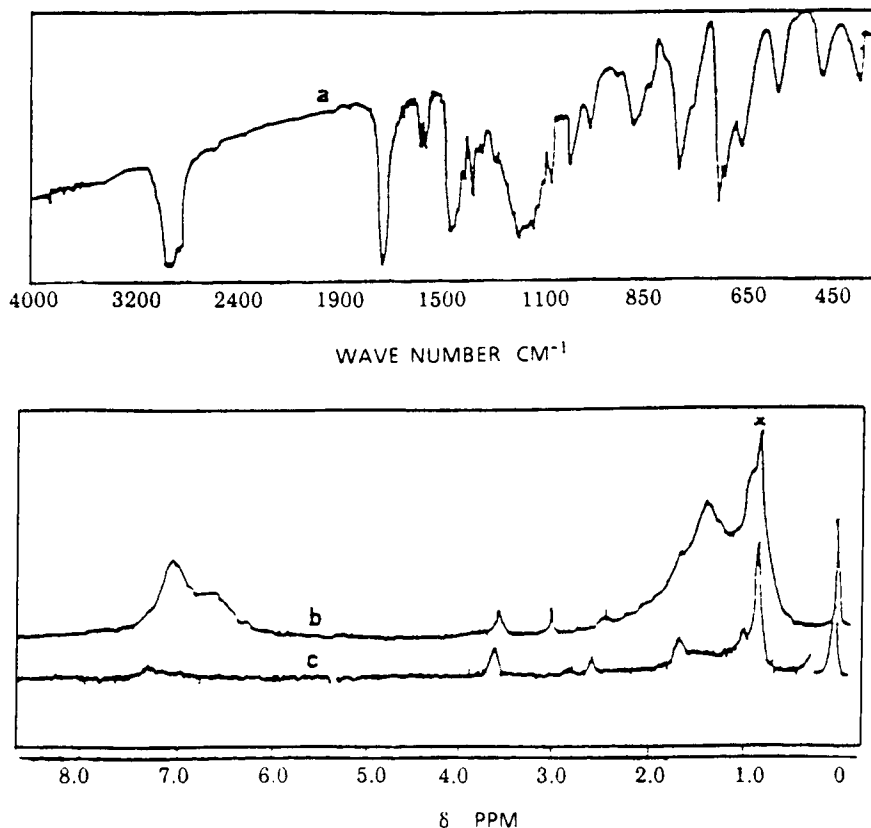
Fig. 4. FT-IR spectrum (a) and ^{1}H-NMR spectrum (b, $F = 0.63$; c, $F = 0.33$, CDCl$_3$) of poly(3-BTS-MMA).

coordination between the empty d orbitals of the tin atom and the π orbitals of the carbonyl or nitrile groups. The stretching absorption bands were found at 502, 505, and 504 cm^{-1} due to the $-$Sn$-$N$=$ group in copoly(3-BTS–AN), and the $-$Sn$-$O$-$ group in copoly(3-BTS–MMA) and copoly(3-BTS–EA), respectively. These frequencies are similar to the following reported values:[10,11] 470–520 cm^{-1} for ν_{Sn-O} and 510 cm^{-1} for ν_{Sn-N}. The bending absorption bands, due to phenyl rings of copoly(3-BTS–MMA), copoly(3-BTS–EA) and copoly(3-BTS–AN), appeared at lower frequencies than those of poly(3-BTS) and copoly(3-BTS–ST), and their absorption intensity was decreased as shown in Table III and Figures 4 and 5.

    IR spectra for homopolymers of AN, VA, MMA and EA, and their copolymers with ST[12,13,14] and 3-BTS, are summarized in Table IV. They exhibit a shift of the stretching vibrations $\nu_{C=O}$, $\nu_{C\equiv N}$, and ν_{C-O-C} to higher frequencies in copoly(3-BTS–MMA), copoly(3-BTS–EA), and copoly(3-BTS–AN) relative to those in poly(MMA), poly(EA), and poly(AN), and in their copolymers with styrene. This suggests that the vibrational modes of the nitrile and the carbonyl group are restricted by the inter- and intramolecular coordination interaction and the vibration of the polarity of the $-$C$=$O and $-$C$\equiv$N groups. The rest of MMA, EA, or AN in a polymeric chain after
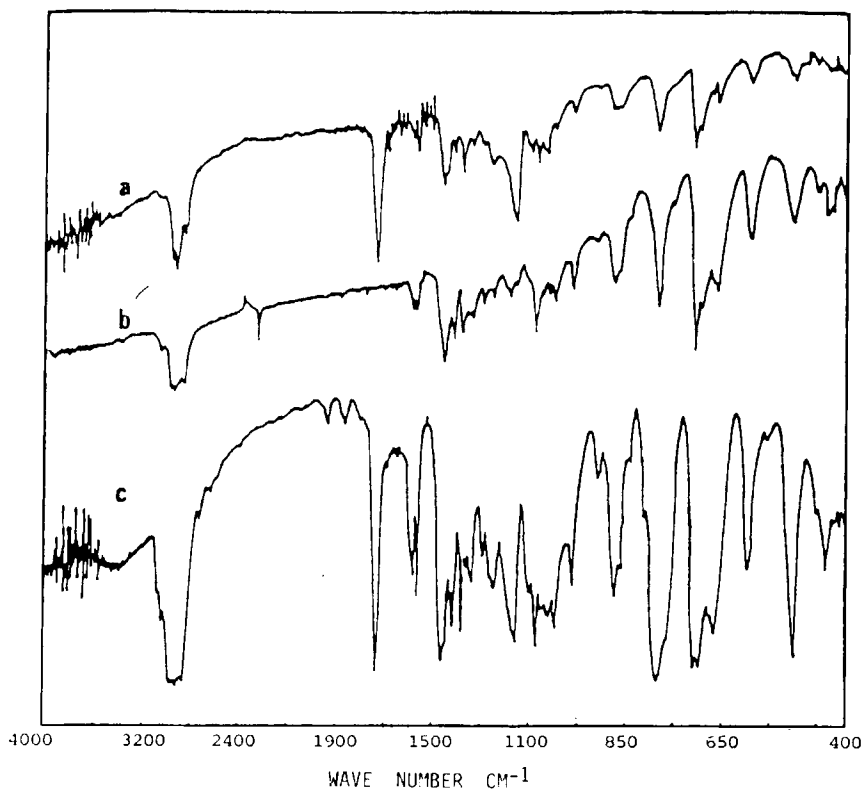
Fig. 5.   FT–IR spectra of poly(3-BTS–EA) (a), –AN (b), and –VA (c).

formation of the inter- and intramolecular coordination are also part of the restriction to vibrational motion. In spite of this coordination, however, we could not find this interaction in the copolymer 3-BTS–VA.

Based on these facts, the mechanism of the copolymerizations between 3-BTS and M_2 (MMA, EA, and AN) is shown in Scheme 2. Inter- and intramolecular coordination is evident from the existence of alternating polymers in copoly(3-BTA–MMA) and copoly(3-BTS–AN). Also, the increase of insolubility in these copolymers, the acceleration of rate of copolymerization, and the increase of conversion yield can be understood by this complexation. The variation of Q_1-e_1 values in copolymers 3-BTS–MMA, 3-BTS–EA, and 3-BTS–AN and the stability of resonance structure by the attack of 3-BTS radical to M_2 are caused by this mechanism.

The ^{1}H-NMR data for copolymers 3-BTS-ST and 3-BTS-MMA are summarized in Table V, and the spectra are shown in Figures 3 and 4. It was observed that homo- and copolymers of 3-BTS obtained were atactic, based on the proton resonances of the ^{1}H-NMR spectra of phenyl rings as shown in Figures 3 and 4.

The proton signals in copoly(3-BTS–ST) appeared almost at the same position as those in poly(3-BTS), due to the charge-transfer mechanism between the phenyl group and the tin atom as shown in Scheme 1, despite the increase of ST content in copoly(3-BTS–ST).

TABLE III
IR Spectral Data (cm⁻¹)

	ν					δ (C—C in PhH)		δ (Ph—H)		ν	
	C≡N	Sn—N	C=O	Sn—O	C—O—C	Mono[c]	Di(meta)[d]	Mono[c]	Di(meta)[d]	H₂C—Sn	Ph—Sn
Poly(3-BTS)[a]							1605 1570 1475		880 780 695	610	440
Copoly(3-BTS—ST)[a]						1600 1500 1455	1600 1570 1475	910 845 760	880 780 695	560	440
Copoly(3-BTS—MMA)[b]			1734	505	1290		1583 1562 1465		870 785 695	596	450
Copoly(3-BTS—EA)[b]			1737	504	1250		1575 1550 1450		875 784 692	592	454
Copoly(3-BTS—VA)[b]			1733	500	1250		1592 1565 1462		875 788 700	596	442
	2289	502					1581 1558 1465		872 787 689	600	450

[a] In film.
[b] By FTIR.
[c] Monosubstituted phenyl ring.
[d] 1,3-Disubstituted phenyl ring.

TABLE IV
IR Spectra for Homopolymers of AN, VA, MMA and EA and Their Copolymers[a] (cm^{-1})

|	AN			VA			MMA			EA		
	H	ST	M[b]	H	ST	M[b]	H	ST	M[b]	H	ST	M[b]
$\nu_{(C\equiv N)}$	2237	2237	2289									
$\nu_{(Sn-N)}$			502									
$\nu_{(C=O)}$				1739	1736	1733	1724	1724	1734	1724	1724	1737
$\nu_{(Sn-O)}$									505			504
$\nu_{(C-O-C)}$				1241	1247	1250	1271	1266	1290	1250	1260	1250

[a] H: Homopolymer, ST: copolymer with ST, M: copolymer with 3-BTS.
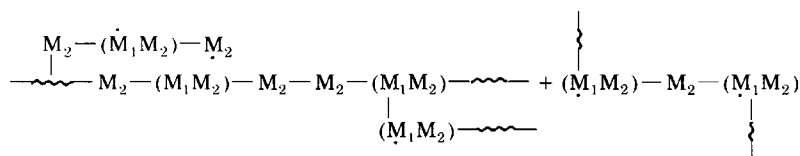[b]: The results of these experiments.

Formation of Intermolecular Coordination:

$$3\text{-BTS} + M_2 \ (\text{MMA, EA, and AN}) \rightleftharpoons \text{Complex} + M_2$$

$$(M_1) \qquad (M_2) \qquad (I)$$
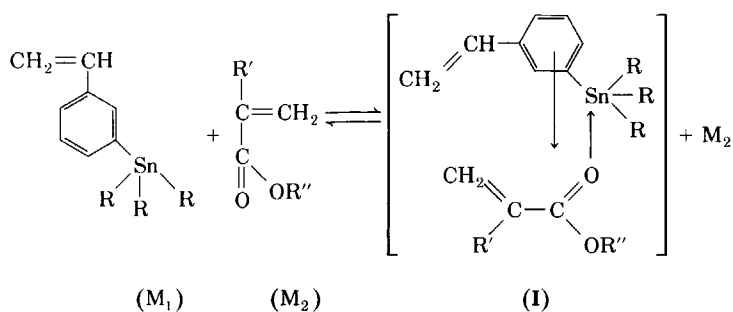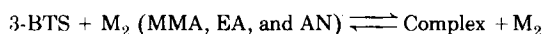
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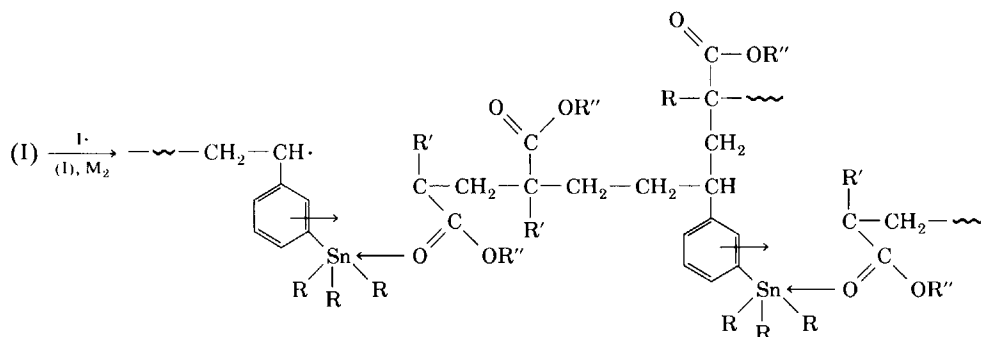
Formation of Crosslinking among Radicals:

where R′ = R″ = CH$_3$ in MMA, R′ = H, R″ = C$_2$H$_5$ in EA, I· = radical of initiator. Poly(3-BTS–AN) is formed by the same mechanism.

Scheme 2.

TABLE V
^{1}H-NMR Spectral Data (ppm)

Assignment	Poly(3 − BTS)[a]	Copoly(3-BTS–ST)[b]	Copoly(3-BTS–MMA)[b]	
			$F = 0.63$	$F = 0.33$
PH—H	7.03	7.07	7.01	7.33
	6.70	6.67	6.63	
—OCH$_3$	–	–	3.47	3.61
			3.01	2.59
			2.43	
—C—CH$_3$	–	–	2.26–0.43	2.21–0.43
CH—CH$_2$— ⎫				
⎬	2.60–0.60	2.60–0.60		
n-C$_4$H$_9$— ⎭				

[a] In CDCl$_3$.
[b] In C$_6$D$_6$.

However, the shift of the proton peaks on the phenyl rings to higher fields in copoly(3-BTS–MMA) points out the electron donating effect from the phenyl groups of 3-BTS to the carbonyl carbon atoms of MMA by inter- and intramolecular coordination. Therefore, the intensity of bending–stretching vibrational absorption bands of the phenyl groups at 1583 and 1465 cm^{-1} in the IR spectra (shown in Fig. 4) are decreased.

The measured values of T_g and T_m in homo- and copolymers of 3-BTS are shown in Table I. In general, T_g depends on the flexibility of the polymer chains and intra- and intermolecular forces. The equilibrium flexibility of the polymer chains is affected by the rotational barriers for the backbone bonds and the steric interactions between the side groups. This flexibility is expected to decrease as the size of the side chain increases, and this would increase T_g. Bulky side groups could also have the opposite effect of decreasing T_g by interfering with efficient chain packing, since this could increase the free volume of the polymer. In Table I, values of T_g in poly(3-BTS), copoly(3-BTS–ST), copoly(3-BTS–MMA), copoly(3-BTS–EA), and copoly(3-BTS–VA) are 82, 66, 90, 95, and 72°C, respectively. The values of T_g for homopolymers of ST, MMA, EA, and VA are 100, 45–105, −24, and 28°C, as taken from the literature.[9].

It was found that copoly(3-BTS–MMA) and copoly(3-BTS–EA) had higher values of T_g than poly(MMA) and poly(EA) because of the inter- and intramolecular coordination. The flexibility of tri-n-butylstannyl group in poly(3-BTS) gives a lower value of T_g than that of poly(ST).[15]

It is well known that the cohesive energy density for solubility is proportional to T_g. The solubility of homo- and copolymers of 3-BTS was decreased with the increase of tin contents in their chains and the resulting changes in cohesive energy density.

The values of T_m were over 300°C in these tin-containing polymers. It has been assumed that these high values are directly related to the presence of the tin atoms.

These materials are being tested for biocidal activity, particularly in marine and agricultural applications.

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