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## Anionic Polymerization of p-Triphenyltin Styrene

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### ABSTRACT

Anionic polymerization of p-triphenyltin styrene (TPSnS) was investigated under high vacuum conditions ( $\sim 10^{-6}$  mmHg). TPSnS has been readily polymerized by sodium naphthalide, potassium naphthalide, or sodium salts of  $\alpha$ -methylstyrene oligomers to form "living polymers" at low temperature ( $\leq -30^\circ\text{C}$ ). The addition of  $\alpha$ -methylstyrene to these living systems gave the block copolymers, TPSnS-block  $\alpha$ -methylstyrene. The Mark-Houwink values of K and a, determined in tetrahydrofuran, were  $K = 0.59 \times 10^{-4}$  and  $a = 0.68$  where M was  $\bar{M}_n$ , indicating that the polymer was moderately coiled in this solvent. Some physical properties of poly(TPSnS) were examined.

### INTRODUCTION

Organic polymers containing tin atoms in the side chains have received considerable attention in respect to both chemical and physical interests. The polymers containing tributyltin esters of carboxylic acid as side chains have become interestingly important for control

of fouling on ship hulls as well as other surfaces in contact with a marine environment [1]. Poly(trialkyltinacrylates) and their methacrylate derivatives are known to be suitable biocidal polymers [2]. Their coating polymers might exhibit special biological properties. Sandler and Tsou [3] have reported that p-triphenyltin styrene present in a copolymer system gives scintillation plastics. The incorporation of the organotin moiety into polymers offers high thermal stabilities and mechanical property improvements of the polymers in some cases [4, 5].

The addition polymerizations of some tin-containing vinyl and acrylate monomers have been studied by radical initiators. These include trialkyltin- and triaryl tinacrylates and methacrylates [6, 7] and p-trialkyltin and p-triphenyltin substituted styrene derivatives [8, 9]. It has been reported that radical initiation of 2-tributylstan-nylbutadiene results in a polymer having a well-defined cis-1,4 structure [10]. Vinyl monomers such as vinyl trimethyltin and vinyl tributyltin have been copolymerized with styrene and methyl methacrylate, but they would not homopolymerize [11].

In contrast, anionic polymerization of organotin monomers is little studied. It was reported that vinyl triethyltin gave a polymer having molecular weight as high as 5000 with n-butyllithium (BuLi) initiation but only in 1% conversion. No reports exist on the anionic polymerization of acrylates and styrene derivatives.

We now report the anionic polymerization of p-triphenyltin styrene and some physical properties of the resulting polymers. Observation regarding the possible incorporation of the monomer into block copolymers is made. Attempts to anionically polymerize p-tributyltin styrene, triphenyltin methacrylate, and  $\beta$ -triphenyltin ethylmethacrylate were unsuccessful.

## EXPERIMENTAL

### Materials

p-Triphenyltin styrene was prepared according to the procedure previously described [8]. The crude product was carefully recrystallized four times from ethanol and dried over  $P_2O_5$  for 48 h under vacuum ( $\sim 10^{-6}$  mmHg). It had a melting point of 110-112°C (literature 112-113°C) [8]. It was identified by IR, NMR, and elemental analysis.

Analysis: Calculated for  $C_{26}H_{22}Sn$ : C, 68.91; H, 4.89. Found: C, 68.73; H, 4.71.

p-Tributyltin styrene was prepared by the procedure similar to that of p-triphenyltin styrene [8]. The crude product was obtained as a viscous liquid in 68% yield. It was purified by using the silica gel (Wakogel C-200) packed column chromatography technique. The purified product was identified by IR, NMR, and elemental analysis.

Analysis: Calculated for  $C_{20}H_{34}Sn$ : C, 61.10; H, 8.72. Found: C, 61.09; H, 8.67.

Triphenyltin methacrylate was prepared as previously described [12], carefully recrystallized three times from n-hexane, and dried over  $P_2O_5$ . It had a melting point of 88–89°C (literature 87.5–88.5°C) [12] and was identified by IR and NMR.

$\beta$ -Triphenyltinethanol was obtained by the following reaction. Triphenyltin lithium, originally prepared from triphenyltin chloride and 2 equivalents of lithium metal in THF, was reacted with ethylene oxide in THF at 30°C to give 80%  $\beta$ -triphenyltinethanol.

$\beta$ -Triphenyltinethyl methacrylate was prepared as follows:  $\beta$ -Triphenyltinethanol, 79 g (0.20 mol), was dissolved in 500 mL of anhydrous THF. The solution was cooled in an ice bath and 14.4 mL (0.18 mol) of pyridine was added. A solution of 16 mL (0.16 mol) of methacrylyl chloride in 50 mL of THF was added dropwise to the rapidly stirred solution. A white precipitate of pyridine hydrochloride immediately precipitated out. The reaction was allowed to continue for 24 h. The reaction mixture was washed with  $NaHCO_3$  saturated aqueous solution,  $NaCl$  saturated aqueous solution, dried over magnesium sulfate, and filtered. Solvent was removed via a rotary evaporator, leaving a slightly yellowish viscous liquid. The residual liquid was purified by using the column chromatography technique. The purified product, obtained in 50% yield with mp 55–57°C, was identified by IR, NMR, and elemental analysis.

Analysis: Calculated for  $C_{24}H_{24}O_2Sn$ : C, 62.24; H, 5.22. Found: C, 62.05; H, 5.22.

Tetraphenyltin was purchased from Wako Pure Chemicals. It was recrystallized two times from benzene, dried over  $P_2O_5$  in vacuo for 48 h, and then sealed in ampules equipped with breakseals as the THF solution. n-Butyllithium was purchased from Wako Pure Chemicals as 15% n-hexane solution. It was sealed in ampules with breakseals as the benzene or n-hexane solution. Sodium naphthalide, potassium naphthalide, sodium salts of  $\alpha$ -methylstyrene living oligomers, and phenyl magnesium chloride were prepared under vacuum according to the usual procedures, and stored in ampules equipped with breakseals as the THF solution.

THF was refluxed over sodium wire and then distilled from  $LiAlH_4$  or sodium naphthalide. Benzene and toluene was washed with concentrated  $H_2SO_4$ , water, 5%  $NaOH$  aqueous solution, water, and dried over  $CaCl_2$ . It was refluxed over sodium wire and then distilled from n-butyllithium. All the reagents used were sealed in individual ampules equipped with breakseals. Monomers were sealed in glassware as a THF or a toluene solution.

$^1H$  NMR spectra were recorded with Hitachi R-24 instrument [  $CDCl_3$  solution and  $(CH_3)_4Si$  as internal standard]. IR spectra were run by using a JASCO IR-G spectrophotometer.

## Procedures

Anionic homo- and copolymerizations were carried out under high vacuum ( $\sim 10^{-6}$  mmHg) in sealed glass reactors on a vacuum line by the method similar to that reported by Pittman [13].

The initiator and monomer solutions were stored in breakseal glass vessels on the vacuum line, and each solution was transferred into the reactor on breaking the seals (the initiator solution was added first). The reaction solutions were stirred by magnetic stirrers and were allowed to stand for 0.5 h at 0 or  $-78^{\circ}\text{C}$ . The polymers were then precipitated by addition to an excess of ethanol. They were filtered, redissolved in THF, and precipitated into ethanol two additional times and were dried by the freeze-dried method.

## Characterization of Polymers

The intrinsic viscosity of polymers was measured in THF at  $40^{\circ}\text{C}$  by using an Ubbelohde viscometer. The universal calibration technique [14] was used to calculate molecular weights and distributions from gel permeation chromatograms and intrinsic viscosity measurements. By this method the Mark-Houwink values of  $K$  and  $a$  were determined. Measurements were carried out at  $40^{\circ}\text{C}$  by using a Toyosoda HLC-802 instrument. Glass transition temperatures ( $T_g$ ) of the polymers were evaluated from the DSC diagrams recorded on a Perkin-Elmer DSC-2 instrument with a 10 deg/min heating rate. Films of polymers were prepared by casting from THF solution or pressing ( $200\text{ kg/cm}^2$ ) at high temperature ( $180^{\circ}\text{C}$ ).

## RESULTS AND DISCUSSION

A series of polymerization of triphenyltin styrene (TPSnS) was carried out with various initiators under high vacuum conditions ( $\sim 10^{-6}$  mmHg). They include BuLi, sodium naphthalide (Na-Nap), potassium naphthalide (K-Nap), sodium salts of  $\alpha$ -methylstyrene oligomers ( $\alpha$ -MeSt-Na), phenyl magnesium chloride (PhMgCl), and lithium aluminum hydride ( $\text{LiAlH}_4$ ). The molecular weights and molecular weight distributions for this series of polymers are listed in Table 1.

BuLi did not initiate polymerization of TPSnS. A low molecular weight material was obtained in 35% yield when a large amount of the initiator was employed. No polymers were produced with either PhMgCl or  $\text{LiAlH}_4$ . The starting material, TPSnS, can be quantitatively recovered in both cases. The reactivities of initiators, PhMgCl and  $\text{LiAlH}_4$ , might be considered to be too weak to initiate the polymerization of styrene derivatives like this monomer [15].

TABLE 1. Polymerization of p-Triphenyltin Styrene (TPSnS) by Anionic Initiators<sup>a</sup>

TPSnS (mmol)	Initiator (mmol)	Solvent (mL)	Temperature (°C)	Conversion (%)	Polymer			
					$\bar{M}_n^b$	$\bar{M}_w^b$	$\bar{M}_w/\bar{M}_n$	
2.00	BuLi	0.062	Toluene	20	-78	0	-	-
2.00	BuLi	0.062	THF	20	-78	0	-	-
0.87	BuLi	0.86	THF	5	-78	35	~1000	-
2.00	$\alpha$ -MeSt-Na	0.071	THF	21	-78	100	15,800	21,900
2.00	K-Nap	0.052	THF	21	-78	100	58,800	124,500
2.00	Na-Nap	0.065	THF	20	-78	100	26,500	41,900
2.00	Na-Nap	0.065	THF	20	-30	100	30,000	50,600
2.00	Na-Nap	0.065	THF	20	0	82	Insoluble	-
2.00	PhMgCl	0.065	THF	20	-78	0	-	-
2.00	LiAlH <sub>4</sub>	0.065	THF	20	-78	0	-	-

<sup>a</sup>All polymerizations were carried out for 0.5 h.<sup>b</sup>Calculated from the universal calibration method.

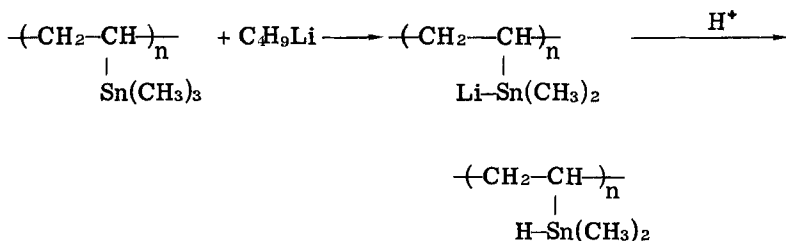
Ready initiation of TPSnS by Na-Nap, and  $\alpha$ -MeSt-Na occurred in THF at  $-78^\circ\text{C}$ . Quantitative yields of soluble polymers with relatively narrow molecular weight distributions were obtained. The reaction mixtures turned immediately a characteristic dark red after addition of the initiators to TPSnS, similar to that observed in well-known living polymerizations of styrene with these initiators [16]. The coloration remained unchanged at  $-78^\circ\text{C}$  even after 24 h. The effect of temperature on the polymerization was, however, critical. At  $0^\circ\text{C}$ , no coloration was observed during the polymerization and significant precipitates were formed which had an IR spectrum similar to the polymers obtained either at  $-78$  or  $-30^\circ\text{C}$ . This swellable material in THF might be a cross-linked polymer because of insolubility in most of the organic solvents.

The resulting polymer was a white solid which was soluble in THF, benzene, and chloroform, and could be cast into a transparent, colorless, and brittle film. The IR spectrum was identical with that of polymer obtained by radical polymerization. The structure was confirmed from the observation that the absorptions connected with the vinyl group are completely absent in the spectra of the polymers, and that the elemental analysis giving reasonable data agree with those calculated.

### BuLi Initiation of TPSnS

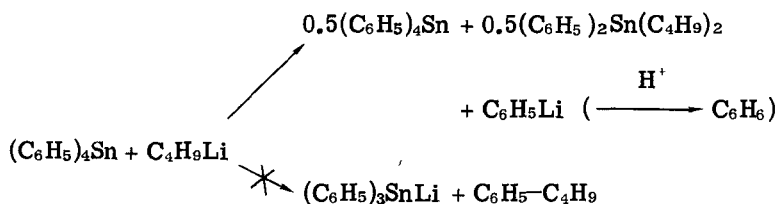
As mentioned before, BuLi did not initiate polymerization either in THF or in toluene under normal polymerization conditions. It gave a low molecular weight oligomer in low yield when the initiator was used at an amount equal to the monomer. These results suggest that BuLi reacts with either the vinyl group or at the Sn-C bonds.

In BuLi-initiated copolymerization of vinyl trimethyltin and styrene, the following reaction was proposed to occur during copolymerization from the fact that the Sn-H bond existed in the copolymer as recognized by the strong absorption of the IR spectrum at  $2035\text{--}75\text{ cm}^{-1}$  [17].



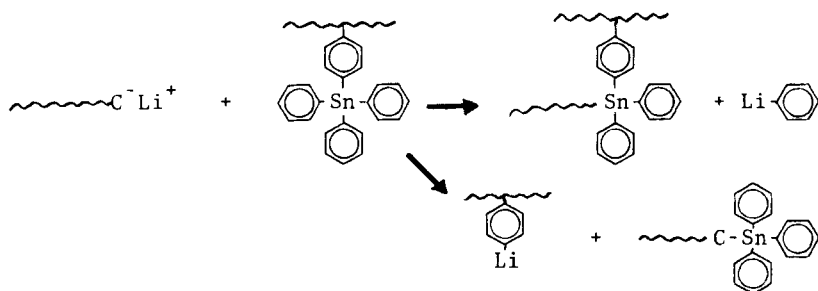
The IR spectrum of the oligomer of TPSnS obtained by BuLi gave no evidence of the existence of the Sn-H bond, indicating that the reaction between TPSnS and BuLi was ruled out in the manner described above.

In order to elucidate the reaction that occurred during polymerization, the reaction of BuLi with  $(\text{C}_6\text{H}_5)_4\text{Sn}$ , a model compound of TPSnS, was performed under identical conditions. The reaction appears to be relatively slow compared to the polymerization, since  $(\text{C}_6\text{H}_5)_4\text{Sn}$  is only slightly soluble in THF at  $-78^\circ\text{C}$ . BuLi and  $(\text{C}_6\text{H}_5)_4\text{Sn}$  (2.9 mmol each) were utilized for the model reaction, and the products isolated included  $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{C}_6\text{H}_5)_2$  (0.8 mmol), benzene (2.1 mmol), and unreacted  $(\text{C}_6\text{H}_5)_4\text{Sn}$  (1.4 mmol). No butylbenzene was recognized on gas chromatographic measurement. Furthermore, Sn-H bond absorption in the reaction mixture was not observed. These facts suggest that the reaction of BuLi with  $(\text{C}_6\text{H}_5)_4\text{Sn}$  takes place in the following manner, although the overall stoichiometry is not satisfied.



It is obvious that the great reactivity of BuLi leads to anion attack at the Sn-C<sub>6</sub>H<sub>5</sub> bonds to some extent.

During the course of the polymerization, if the same anion attack at the Sn-C<sub>6</sub>H<sub>5</sub> bond in the polymer occasionally occurred, it would result in chain transfer or chain termination reactions, branch points being introduced as follows:



This would also account for the fact that significant amounts of cross-linked polymers were formed with sodium naphthalide at  $0^\circ\text{C}$ .



TABLE 2. Polymerizations of p-Tributyltin Styrene (TBSnS), Triphenyltin Methacrylate, and  $\beta$ -Triphenyltinethyl Methacrylate<sup>a</sup>

Monomer	mmol	Initiator	mmol	THF (mL)	Polymer (%)
TBSnS	1.54	Na-Nap	0.144	15	Trace
TBSnS	1.27	$\alpha$ -MeSt-Na	0.060	15	Trace
Triphenyltin methacrylate	2.14	Na-Nap	0.082	10	Insoluble material 8
Triphenyltin methacrylate	2.77	LiAlH <sub>4</sub>	0.064	20	Insoluble material 18
Triphenyltin methacrylate <sup>b</sup>	2.58	LiAlH <sub>4</sub>	0.230	20	Insoluble material 24
$\beta$ -Triphenyltinethyl methacrylate	2.39	Na-Nap	0.120	12	56 <sup>c</sup>
$\beta$ -Triphenyltinethyl methacrylate	2.38	LiAlH <sub>4</sub>	0.160	10	9 <sup>c</sup>
$\beta$ -Triphenyltinethyl methacrylate	2.10	PhMgCl	0.170	10	20 <sup>c</sup>

<sup>a</sup> All polymerizations were carried out at -78° C for 5 h.

<sup>b</sup> A polymerization was carried out at -123° C for 5 h.

<sup>c</sup> Molecular weights of polymers were 10,000-20,000 which were estimated by GPC diagrams.

Anionic Polymerizations of p-Tributyltin Styrene, Triphenyltin Methacrylate, and  $\beta$ -Triphenyltinethyl Methacrylate

Anionic polymerizations of three additional tin-containing monomers were carried out with Na-Nap,  $\alpha$ -MeSt-Na,  $\text{LiAlH}_4$ , and  $\text{PhMgCl}$  in THF at  $-78^\circ\text{C}$ . The results are summarized in Table 2.

p-Tributyltin styrene (TBSnS) did not appear to undergo polymerization under the conditions where TPSnS polymerized readily. The reaction mixtures turned immediately dark green or dark blue after the addition of TBSnS to Na-Nap or  $\alpha$ -MeSt-Na, respectively. The color remained during the reactions and disappeared upon contact with air, resulting in only a trace of polymers. Since it is well established that the Sn-alkyl bond is less stable toward strong nucleophilic compounds than the Sn-aryl bond, it is possible to assume that the nucleophilic attack of initiators takes place at the Sn-butyl bond instead of vinyl group of TBSnS [18]. Thus the effect of the substituent bonded to a tin atom on anionic polymerization appears to be critical.

The anionic polymerization of triphenyltin methacrylate with Na-Nap or  $\text{LiAlH}_4$  resulted in low conversion. Lowering the temperature ( $-123^\circ\text{C}$ ) had little effect. In both cases, most monomer was recovered along with 8-24% of insoluble materials which had an IR spectra similar to the monomer except for the disappearance of the bands based on the vinyl group. The materials were insoluble in most of organic solvents and therefore seemed to be cross-linked polymers.

Polymerization of  $\beta$ -triphenyltinethyl methacrylate appeared similar. The products from this monomer were, however, soluble in benzene, THF, and DMF. These products were shown by GPC measurements to have molecular weight of 10,000-20,000. These results strongly suggest that significant reactions causing chain transfer or termination occur during the course of the polymerization of both tin-containing methacrylate monomers.

Molecular Weights and Polydispersities of Poly-(TPSnS)

The dependence of molecular weight on the monomer-to-initiator ratio for the Na-Nap initiation system is listed in Table 3. The molecular weight increased as the monomer-initiator ratio increased. There is good agreement between the experimental values of molecular weight and those calculated from the monomer-to-initiator ratios (Fig. 1). Additionally, after depletion of the monomer supply, the resulting polymeric anions were observed to retain their activities from the demonstration that postaddition of the fresh monomer to polymer anion gave a large increase in viscosity and, after work-up, 100% conversion to polymer. The GPC curves of both fractions showed that postaddition polymerization occurred to give higher molecular

TABLE 3. Effect of TPSnS:Na-Nap Ratio on Molecular Weight<sup>a</sup>

TPSnS (mmol)	Na-Nap (mmol)	THF (mL)	$\frac{[M]}{[I]}$	Conversion (%)	$[\eta]^b$	$\bar{M}_n^c$	$\bar{M}_w^c$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ calculated
1.00	0.049	10	20.4	100	0.050	19,800	35,500	1.80	15,700
2.00	0.065	20	30.8	100	0.066	26,500	41,900	1.68	24,400
1.90	0.046	20	41.3	100	0.081	35,800	60,200	1.68	32,600
1.97	0.032	20	61.6	100	0.090	38,900	69,400	1.78	47,100
2.00	0.020	20	100	100	0.141	82,000	138,000	1.68	90,400
1.00	0.048	10	20.8	100	0.049	19,900	35,000	1.76	16,000
0.90 <sup>d</sup>	-	10	39.6	100	0.080	34,000	56,000	1.65	32,000

<sup>a</sup>All polymerizations were carried out at -78°C for 0.5 h.

<sup>b</sup>Measured in THF at 40°C.

<sup>c</sup>Calculated from the universal calibration method.

<sup>d</sup>0.90 mmol of fresh TPSnS was added to a reaction mixture of 1.00 mmol of TPSnS and 0.048 mmol of Na-Nap in THF.

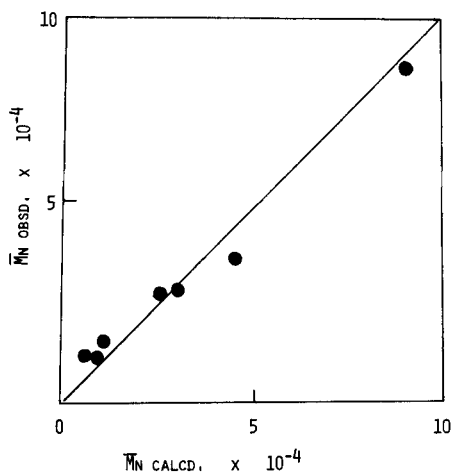


FIG. 1. The relationship between  $\bar{M}_n$  observed and  $\bar{M}_n$  calculated of the polymers obtained by anionic polymerization of TPSnS by Na-Nap in THF at  $-78^\circ\text{C}$  for 0.5 h.

weight polymer without a shoulder. The molecular weight observed was found to be in good agreement with that calculated. This strongly suggests that the anionic polymerization of TPSnS is a living polymerization. It follows that poly(TPSnS) of any desired molecular weight can be made.

The molecular weight distributions were characterized by the  $\bar{M}_w/\bar{M}_n$  ratios calculated from the GPC diagrams and were in most cases somewhat broad in comparison with those reported in anionic living polymerizations of styrene and  $\alpha$ -methylstyrene under carefully controlled conditions [19].

### Block Copolymers Containing Poly(TPSnS) Units

The lack of a termination reaction and the remaining activity of the resulting polymer anion after depletion of the monomer supply have been demonstrated before in the anionic polymerization of TPSnS in THF at  $-78^\circ\text{C}$ . It is possible that the utilization of this polymeric anion as an initiator of polymerization of second monomers results in the preparation of new block copolymers containing poly(TPSnS) units.

Thus living poly(TPSnS) was prepared and used to initiate  $\alpha$ -methylstyrene. When  $\alpha$ -methylstyrene was added to the living polymeric dianion of TPSnS, originally prepared by Na-Nap initiation in THF at

TABLE 4. Block Copolymerization of TPSnS with  $\alpha$ -Methylstyrene by Use of Poly(TPSnS) Dianions<sup>a</sup>

Run	Addition	TPSnS (mmol)	$\alpha$ -MeSt (mmol)	Na-Nap (mmol)	THF (mL)	Time (h)	Conversion (%)	$[\eta]^b$	$\bar{M}_n^c$	$\bar{M}_w^c$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ calculated
1	First	1.52	-	0.054	15	0.5	100	0.064	24,000	48,800	2.03	23,200
	Second	(3.58) <sup>d</sup>	4.99	(0.127) <sup>d</sup>	40	18.5	100	0.230	38,500	108,000	2.81	32,400
2	First	2.50	-	0.040	25	0.5	100	0.094	40,500	66,500	1.65	47,000
	Second	(2.54) <sup>e</sup>	6.16	(0.041) <sup>e</sup>	40	5.0	99	0.387	88,000	150,000	1.74	90,000

<sup>a</sup>All polymerizations were carried out -78°C.<sup>b</sup>Measured in THF at 40°C.<sup>c</sup>Calculated from the universal calibration method.<sup>d</sup>4.99 mmol of  $\alpha$ -methylstyrene was added to a reaction mixture of 3.58 mmol of TPSnS and 0.127 mmol of Na-Nap in THF.<sup>e</sup>6.16 mmol of fresh  $\alpha$ -methylstyrene was added to a reaction mixture of 2.54 mmol of TPSnS and 0.041 mmol of Na-Nap in THF.

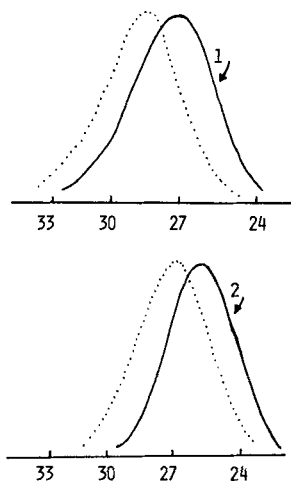


FIG. 2. GPCs of seed poly(TPSnS) and block copolymers formed upon post-addition of  $\alpha$ -methylstyrene: (···) initial seed poly(TPSnS), (—) block copolymers 1 and 2 (Table 4).

$-78^{\circ}\text{C}$ , the viscosity increased and a quantitative yield of polymer was obtained. These polymerizations are summarized in Table 4 and the GPC curves are shown in Fig. 2.

The GPC curves showed that the peaks of the starting poly(TPSnS) symmetrically displaced toward higher molecular weights after addition of  $\alpha$ -methylstyrene. The observed values of  $\bar{M}_n$  of the final polymers were in reasonable agreement with those expected from the initiator-to-monomer ratio. This clearly indicates that the starting poly(triphenyltin styryl) dianion is capable of initiating polymerization of  $\alpha$ -methylstyrene to form an ABA-type block copolymer of  $(\alpha\text{-methylstyrene})_y(\text{TPSnS})_x(\alpha\text{-methylstyrene})_y$ .

Similarly, the ABA-type block copolymers, TPSnS block styrene, TPSnS block isoprene, TPSnS block butadiene, TPSnS block methyl methacrylate, and TPSnS block acrylonitrile were made using poly(triphenyltin styryl) dianions in THF at  $-78^{\circ}\text{C}$ . Their detailed experimental results and physical properties will be reported in a subsequent paper.

### Some Properties of Poly(TPSnS) and Poly(TBSnS)

Poly(TPSnS) is soluble in the organic solvents benzene, toluene, THF, 1,4-dioxane, chloroform, dichloromethane, chlorobenzene, acetonitrile, methyl iso-butyl ketone, and N,N-dimethylformamide,

TABLE 5. Glass Transition Temperatures ( $T_g$ ) and Softening Points for Poly(p-triphenyltin styrene), Poly(p-tributyltin styrene), Poly(p-trimethyltin styrene), and Random Copolymers of p-Triphenyltin Styrene-Styrene, and p-Tributyltin Styrene-Styrene

Polymers	$T_g$ ( $^{\circ}\text{C}$ )	Softening point ( $^{\circ}\text{C}$ )	Refs.
Poly(TPSnS)	176-180	220-230	This work
Poly(TBSnS)	<sup>a</sup>	65-70	This work
Poly(TMSnS)	-	170-180	[ 9 ]
Poly(styrene)	80-90	-	[ 22 ]
Copoly(TPSnS-styrene) <sup>b</sup>	157	170	This work
Copoly(TBSnS-styrene) <sup>c</sup>	48	65-70	This work

<sup>a</sup>The value of  $T_g$  could not be measured by DSC measurement. It was estimated to be below room temperature ( $\leq 25^{\circ}\text{C}$ ) by its softening point.

<sup>b</sup>The copolymer was obtained by the radical route. The ratio of TPSnS to styrene in the copolymer was a 50/50 mol ratio.

<sup>c</sup>The copolymer was obtained by the radical route. The ratio of TBSnS to styrene in the copolymer was a 20/80 mol ratio.

but insoluble in n-hexane, acetone, methanol, and ethanol. Poly-(TBSnS) obtained by the radical route is readily dissolved in all the above solvents except methanol.

To examine the behavior of poly(TBSnS) in solution, the intrinsic viscosities and molecular weights of poly(TPSnS) were correlated by the Mark-Houwink equation,  $[\eta] = KM^a$  [20, 21]. The correlation was made for  $\overline{M}_n$ , although the samples used were of relatively broad distributions ( $\overline{M}_w/\overline{M}_n = 1.5-2.0$ ). The following relation was obtained:

$$[\eta] = 0.59 \times 10^{-4} M^{0.68}$$

The value of the exponent in the above equation compares favorably with that of the corresponding viscosity molecular weight relation for polystyrene in the same solvent ( $a = 0.70$ ). The moderate agreement in both values suggests that the polymer of TPSnS is coiled, similar to that reported previously for polystyrene [23].

To evaluate the thermal stability, comparative values of  $T_g$  and softening points were obtained for poly(TPSnS), poly(TBSnS), and

random copolymers of TPSnS-styrene and TBSnS-styrene, respectively. The results are summarized in Table 5. The value of  $T_g$  for poly(TPSnS) is quite high and comes very close to those of poly( $\alpha$ -methylstyrene) and poly(2,4,6-trimethylstyrene) [23]. Poly(TPSnS) had a softening point of 220-230°C. It was reported that poly(p-trimethyltin styrene) had a softening point in the range of 170-180°C [8]. Unlike these tin-containing styrene polymers, poly(TBSnS) exhibited a very low softening point, from which the  $T_g$  for this polymer is estimated to be below room temperature. The  $T_g$  and softening points of random copolymers were shown to be between those of polystyrene and the organotin homopolymers.

Finally, poly(TPSnS) can be cast from THF solution or in finely divided form pressed into transparent, colorless, and brittle films or sheets at an elevated temperature (180°C) and pressure (200 kg/cm<sup>2</sup>).

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