

## Synthesis of poly{4-[bis(trimethylstannyl)methyl]styrene} and its properties for electron-beam resist

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### Summary

To create high performance resist materials, synthesis of novel organostannun-containing polymer was investigated. 4-[Bis(trimethylstannyl)methyl]styrene (BSnMS) was synthesized by a reaction between trimethylstannyl chloride and 4-vinylbenzyl lithium that was prepared through a metalation reaction of 4-methylstyrene by lithium diisopropylamide. Radical polymerization of BSnMS proceeded smoothly to give a polymer. Glass transition temperature of poly(BSnMS) ( $T_g=140^\circ\text{C}$ ) was fairly high among polystyrene homologues. Poly(BSnMS) thus obtained showed naga-working properties toward EB exposure. Sensitivity of the poly(BSnMS) was  $9.0 \sim 9.6 \text{ mC cm}^{-2}$ , keeping high  $\gamma$ -value ( $3.2 \sim 4.9$ ).

### Introduction

Tendency to grow smaller patterns of electron devices have given needs to explore high performance resists for submicron lithography. Electron beam (EB) resist is one of the promising technologies for nanometer dimension. To get high resolution patterns, very thin resist film must be used. For this purpose, however, organic polymers have not enough resistivity against  $\text{O}_2$  reactive ion etching ( $\text{O}_2$  RIE). Organosilicon-containing polymers are being considered as one of the candidates for materials with high resistivity against  $\text{O}_2$  RIE, the mechanism of which is as follows (1-2): When the etching started, surface of the Si-containing polymer reacted immediately with oxygen to form  $\text{SiO}_2$  thin layer on the surface. The  $\text{SiO}_2$  thin layer thus formed prevents further etching by  $\text{O}_2$  RIE. Such organosilicon-containing polymer resists, however, have several problems. For example, organosilicon group itself shows not so high sensitivity against EB exposure. To improve the sensitivity, introduction of EB-sensitive groups into the polymer by certain technique such as copolymerization must be done. Such a copolymerization, however, induces to lower resolution of the resist sometimes (3). In addition, the resist with the  $\text{SiO}_2$  thin layer is hard to remove under mild conditions after the etching finished (4). Recently, organogerman- and stannun-containing polymers become attractive to solve the above problems (4-6).

Last several years, we have been focusing on creation of organometallic polymers having new structure through new synthetic routes (7-10). Structure-function relations of these polymers have also been investigated (3)(10-11). Recently, our new polymers were found to show unique characteristics as EB resist. For example, poly[4-{bis(trimethylsilyl)methyl}styrene], poly(BSiMS), showed nega-working resist materials against EB exposure (3) with extremely high contrast parameter ( $\gamma=8.1$ ). The sensitivity of the poly(BSiMS), however, was not so high ( $D_g^{0.5}=30 \mu\text{C cm}^{-2}$ ). To improve the sensitivity, we started to investigate EB resist properties of organostannun-containing polymers. The objective of this work was to create new organostannun-containing polymers with high performance as resist materials. For the purpose, we synthesized new Sn-containing polymer with the same skeleton as that of poly(BSiMS). Our hypothesis was such a skeleton to play an important role for unique characteristics for EB resist. This paper deals with synthetic route for poly[4-{bis(trimethylstannyl)methyl}styrene], poly(BSnMS). Properties of poly(BSnMS) as EB resist are also described.

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## Experimental

All procedures on synthesis and polymerization of Sn-containing monomer were carried out under purified argon to eliminate oxygen and moisture.

### Materials

Commercial tetrahydrofuran (THF), diisopropylamine (DPA), 4-methylstyrene (MST), trimethylstannyl chloride (TMSnCl), benzene, and methanol were purified by conventional method (12). Butyllithium was used as hexane solution, the concentration of which was determined by Gilman's double titration method (13-14). 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Commercial methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) were used as received.

### Synthesis of 4-[bis(trimethylstannyl)methyl]styrene (BSnMS)

One of the representative procedures of synthesis of BSnMS is described. To a stirred THF solution (21.1 ml) of DPA (1.01 g; 10.0 mmol), a hexane solution of butyllithium (3.1 ml; 5.0 mmol; 1.6 mol dm<sup>-3</sup>) was added in a 100 ml round-bottomed flask equipped with a 3-way stopcock. After stirring for a few minutes to complete the formation of lithium diisopropylamide (LDA), MST (0.03 g; 2.5 mmol) was added by using a syringe. The color of the mixture was observed to turn yellow immediately. Then, TMSnCl (1.0 g; 5.0 mmol) was added by a syringe, and the reaction mixture was allowed to react at 20 °C for 15.5 h. The mixture was analyzed directly by gas chromatography toward MST, 4-(trimethylstannylmethyl)styrene (SnMS), and 4-[bis(trimethylstannyl)methyl]styrene (BSnMS). The concentrations of an oligomer formed were calculated from number-average molecular weights and yields, which were determined from GPC results, assuming refractive indexes of the oligomeric products were constant. Purification of BSnMS was carried out by fractional distillation over calcium hydride under reduced pressure (93 °C / 0.1 mmHg).

### Anionic Polymerization of BSnMS

A glass wall of a 100 ml-round bottomed flask was carefully washed with hexane solution of butyllithium, then, the entire solution was removed by a syringe. Into the flask, THF (10 ml), BSnMS (4.2 ml; 10 mmol) and hexane solution of butyllithium (0.26 ml; 0.44 mmol; 1.7 mol dm<sup>-3</sup>) were added by using a syringe. The color of the mixture was observed to turn brownish red immediately. The mixture was allowed to react for 20 min at 20 °C, then, small amount of methanol was added to quench the reaction. The mixture was analyzed directly by gel permeation chromatography (GPC) to determine the conversion of BSnMS, then poured into large excess amount of methanol. The precipitate was purified by 3-fold successive precipitations from THF solution into methanol. The polymer sample collected was subjected to freeze-drying with benzene to remove solvents employed.

### Radical Polymerization of BSnMS

One of the representative procedures of radical polymerization of BSnMS is described. Benzene (36 ml), 2, 2'-azobisisobutyronitrile (AIBN) (30 mg; 0.18 mmol) and BSnMS (9.5 g; 21.5 mmol) were filled in a glass tube. After sealing off the tube under high vacuum, the mixture was allowed to react at 60 °C for 24 h, then the tube was opened. The polymer obtained was dissolved in THF and poured into methanol. Precipitates formed were purified by 3-fold successive reprecipitations from THF solution into methanol. The polymer sample collected was subjected to freeze-drying with benzene to remove the solvents employed.

### Resist Processing

One of the representative procedures of resist processing is described. On a Si wafer, MIBK solution of the polymer (10 wt-%) was coated by using a spinner. The resist films thus

obtained were prebaked at 120 °C for 15 min to yield a layer in 0.4 μm. Exposure was carried out on SEM at 20 kV. The range of dose was from 1 to 300 μC cm<sup>-2</sup>. The wafer was developed by soaking in MIBK solution for 1 min and then rinsed by dipping in solution of MIBK/IPA = 1/1 (v/v) for 1 min and in IPA for 1 min. Remaining film thicknesses were measured with an interferometer. Data were handled in the usual manner (15-16). A lithographically useful sensitivity is represented by the dose required to produce half relative thickness, D<sub>g</sub><sup>0.5</sup>. A contrast parameter, γ, was defined according to the literature (16) as follows:  $\gamma = 0.5 \log(Dg^{0.5}/Dg^i)^{-1}$ , where D<sub>g</sub><sup>i</sup> was defined as a minimum EB dose for detectable gel formation.

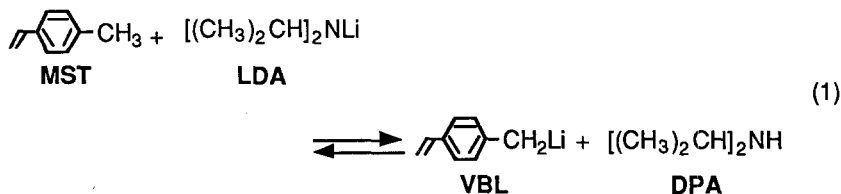
### Measurement

<sup>1</sup>H NMR Spectra were observed on a JEOL EX400 spectrometer at room temperature, using a 5mm glass tube containing a solution of the polymer sample in CDCl<sub>3</sub> (1.0g dl<sup>-1</sup>). Gas chromatograms were taken with a Hewlett Packard 5890. For gel permeation chromatography (GPC) measurement, a Toyo Soda HLC-8020 was used (column: TSK-Gel G4000H8+G3000H8+G2500H8) to determine number-average molecular weight ( $\bar{M}_n$ ) and weight-average molecular weight ( $\bar{M}_w$ ). Glass transition temperatures of the polymers were determined by using a differential scanning calorimeter (DSC) (Mettler TA4000 system) at a heating rate of 20 °C min<sup>-1</sup> from -100 °C to 200 °C. EB exposures were carried out by a scanning electron microscope (Hitachi S-5000A) at 20 kV. Film thicknesses were measured by an interferometer (Dainihon Screen Lambda A).

## Results and discussion

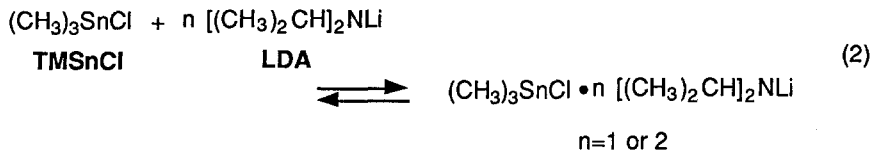
### Synthesis of BSnMS

We found previously that lithium diisopropylamide (LDA) induced a metalation reaction of 4-methylstyrene (MST) to form 4-vinylbenzylithium (VBL) without any side reaction such as polymerization at least 30 min in THF at 20 °C [Eq.(1)] (8). Equilibrium constant for Eq.(1)



was determined to be 0.54 in THF at 20 °C. VBL can be regarded as unique carbanion having polymerizable vinyl group and used as an intermediate for several new monomer syntheses (7). To synthesize Si-containing monomers, organosilyl chloride was used for coupling reaction with VBL. In this stage, it is important to drop the SiCl compound slowly into the reaction system containing VBL and LDA, to avoid it to react with LDA. Actually, when trimethylsilyl chloride (TMSCl) was dropped into the system, TMSCl reacted predominantly with VBL than LDA to form 4-(trimethylsilylmethyl)styrene (SiMS), owing to steric hindrance between TMSCl and LDA. The SiMS was metalated again by LDA, and finally, the metalated SiMS reacted with TMSCl to form 4-[bis(trimethylsilyl)methyl]styrene (BSiMS). This way, doubly trimethylsilylated monomer was obtained easily by one-pot from MST as a starting material. Yield of BSiMS attained up to 65 % under appropriate reaction conditions.

To synthesize Sn-containing monomers, trimethylstannyl chloride (TMSnCl) was used as coupling agent with VBL. In this case, we found that a coupling reaction between TMSnCl and LDA did not proceed easily in THF, but formed a complex between them [Eq.(2)] (17).



Therefore, TMSnCl needs not to drop slowly into the reaction system containing VBL and LDA. Figure 1 shows, change in concentrations of stannylation products as a function of time. As can be seen in the figure, concentration of mono-trimethylstannylated MST [4-(trimethylstannylmethyl)styrene, SnMS] (18) increased in the initial stage, then doubly trimethylstannylated MST (4-[bis(trimethylstannyl)methyl]styrene, BSnMS) (18) increased until 16 h, indicating this system to be one of the typical consecutive reactions. On the basis of these results, it can be summarized that the present synthetic reactions proceed as follows: First of all, free LDA reacts with MST to form VBL, then, VBL reacts with free TMSnCl to form SnMS. By consumption of free LDA and TMSnCl, they produce again from the LDA/TMSnCl complex. This mechanism prevents the formation of coupling product between LDA and TMSnCl, though certain amount of oligomer was formed during the reaction. Under the appropriate reaction conditions, yield of the BSnMS was attained up to 50 % (19).

#### *Polymerization of BSnMS and Its Thermal Property*

To examine a polymerizability of the Sn-containing monomers, polymerizations of BSnMS using anionic and radical initiators were carried out, results of which are summarized in Table 1. When butyllithium was used as an initiator, polymerization of BSnMS took place to form a polymer having the number average molecular weight of  $1.2 \cdot 10^4$ , though expected molecular weight calculated from initial [monomer]/[initiator] ratio was  $1.0 \cdot 10^4$ . From GPC trace of the

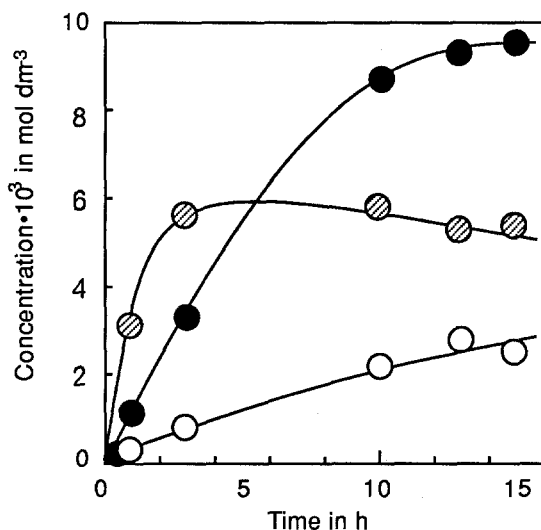


Fig.1 Change in concentrations of the products obtained from the stannylation reaction of 4-methylstyrene with trimethylstannyl chloride (TMSnCl) catalyzed by lithium diisopropylamide (LDA) as a function of time.  $\textcircled{hatched}$ : SnMS;  $\bullet$ : BSnMS;  $\circ$ : Oligomer. (The same reaction conditions as in Experimental part)

Table 1. Results on polymerizations of 4-[bis(trimethylstannyl)methyl]styrene (BSnMS)

Initiator	[BSnMS] <sub>0</sub> in mol dm <sup>-3</sup>	[Initiator] <sub>0</sub> in mmol dm <sup>-3</sup>	Solvent	Temp. in °C	Time in h	Yield in %	$\bar{M}_n \cdot 10^{-4}$	$\bar{M}_w/\bar{M}_n$
BuLi	1.0	44	THF	20	0.33	96	1.2	2.87
AIBN	0.6	5	Bz	60	24	40	5.1	1.89

polymer obtained (Figure 2), molecular weight distribution of poly(BSnMS) was relatively larger ( $\bar{M}_w/\bar{M}_n=2.87$ ), indicating some wrong reactions such as chain transfer reactions took place during the polymerization. Actually, <sup>1</sup>H NMR spectrum of the polymer showed several signals around 0 ppm though the signal of Sn-CH<sub>3</sub> is essentially singlet for normal vinyl polymer of BSnMS. This may be due to the weak Sn-C bond in BSnMS against nucleophilic attacks. Radical polymerization of BSnMS proceeded smoothly to give a polymer having the number average molecular weight of  $5.1 \cdot 10^4$  ( $\bar{M}_w/\bar{M}_n=1.89$ ) (Figure 2.(b)). The poly(BSnMS) thus obtained was dissolved in several organic solvents such as benzene, THF, chloroform, MIBK, etc. Figure 3 shows <sup>1</sup>H NMR spectrum of the poly(BSnMS) thus obtained. According to the intensity ratios and the assignments of the signals referred to polystyrene and BSnMS monomer, it is found the polymer to be obtained through normal addition polymerizations.

We reported previously (3) that glass transition temperature (T<sub>g</sub>) of poly(SiMS) (82 °C) was lower than that of poly(MST) [93 °C (20)] probably due to the movement of methylene linkage between phenyl and trimethylsilyl group. Introduction of second trimethylsilyl group at the same carbon atom showed a significant increase of glass transition temperature, over 70 °C (T<sub>g</sub> of poly(BSiMS) ≥ 150 °C) (3). Fairly high T<sub>g</sub> of poly(BSiMS) originated from its skeleton is one of the reasons to show high contrast parameter (γ) as EB resist. The Sn-containing polymers have the same tendency as the Si-containing polymers although T<sub>g</sub> of the former (T<sub>g</sub>=140°C) is slightly lower than that of the latter. These facts indicate that the skeleton of chain branching at para-position of phenyl ring in polystyrene plays an important role to

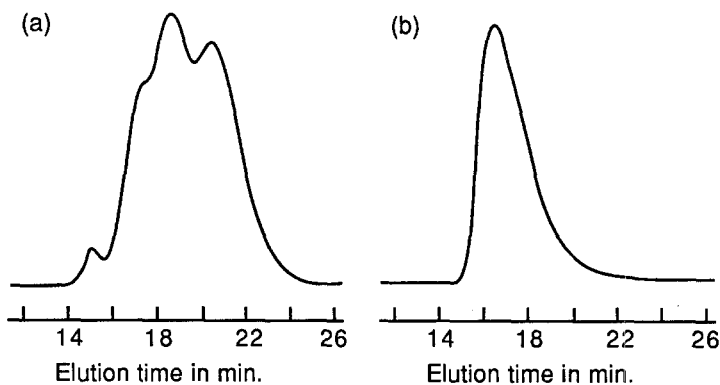


Fig.2 Gel permeation chromatograms of poly(BSnMS) formed by (a) an anionic polymerization and (b) a radical polymerization. (The same conditions as in Table 1)

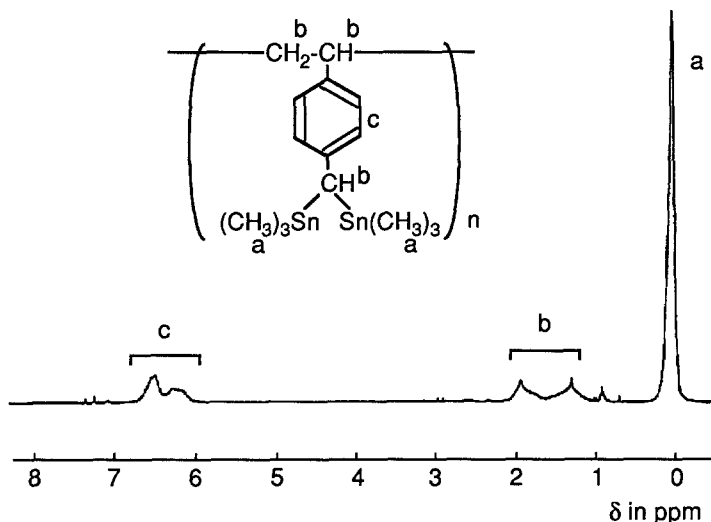


Fig.3 <sup>1</sup>H NMR spectrum of poly(BSnMS) formed by radical polymerization. (The same sample as in Figure 2. (b) (a:18.2H; b:4.2H; c:4.0H)

suppress mobility of the polymer. Such a high T<sub>g</sub> let us anticipate the poly(BSnMS) also to show high γ-value.

Thermogravimetric analysis (TGA) made a clear difference between Si- and Sn-containing polymers. Figure 4 shows TGA curves of poly(BSiMS) and poly(BSnMS) under argon atmosphere. As can be seen in the figure, the weight loss of poly(BSiMS) started around 300 °C to attain 100%-weight loss at 450 °C, indicating complete decomposition to take place probably due to the depolymerization of the polymer. In contrast, the weight loss of

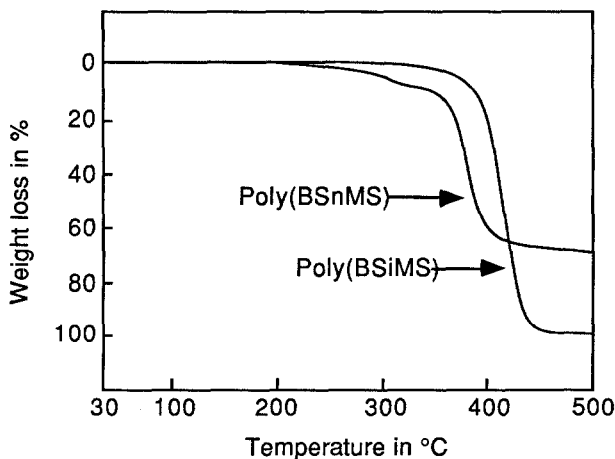


Fig. 4 TGA curves of poly(BSiMS) and poly(BSnMS)

poly(BSnMS) started around 200 °C, and 30% of the polymeric materials remained even at 500 °C, indicating some strange reactions to proceed owing to low bond energy of C-Sn bond.

#### Properties of Poly(BSnMS) as EB Resist Materials

As the poly(BSnMS) has the structure similar to poly(BSiMS), a high stannum content (53.6 wt-%), and a fairly high glass transition temperature (140 °C) as stated above, the polymer was of interest as resist materials. Characteristics of the poly(BSnMS) for EB resist were investigated using SEM at 20 kV.

Figure 5 shows characteristic curves for poly(BSnMS)s toward EB exposure. With EB-exposure, the polymers were insolubilized, meaning the polymers also to work as nega-working resists. Lithographic parameters determined from the curves are summarized in Table

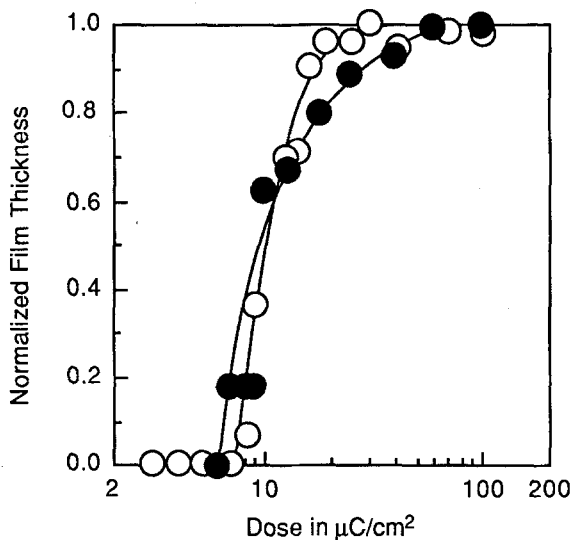


Fig.5 Sensitivity characteristic curves of poly(BSnMS)s as an electron-beam resist. ●:  $\overline{M}_w/\overline{M}_n=1.89$ ; ○:  $\overline{M}_w/\overline{M}_n=1.18$ .

Table 2 Properties of Si- and Sn-containing polymers as electron-beam resist materials

Polymer	$\overline{M}_w \cdot 10^{-4}$	$\overline{M}_w/\overline{M}_n$	Tg in °C	$D_{g^{0.5}}$ in $\mu\text{C}/\text{cm}^2$	$D_{g^1}$ in $\mu\text{C}/\text{cm}^2$	$\gamma$
Poly(BSnMS)	9.7	1.89	n.d.	9.0	6.3	3.2
Poly(BSnMS) <sup>a)</sup>	15.4	1.18	140	9.6	7.7	4.9
Poly(BSiMS) <sup>b)</sup>	10.6	1.17	156	30	26	8.1

a) Further fractional precipitation of poly(BSnMS) prepared by radical polymerization was carried out.

b) Ref. 3

2. As anticipated, an introduction of organostannyl group increased sensitivity toward EB-exposure, owing to the high linear energy transfer (LET) and reactivity of polar organostannyl groups against the electron beam (5). This may induce the crosslinking reaction around the chain branching in addition to methine in the main chain. Such complicated crosslinking mechanisms made the contrast parameter lower slightly than that of poly(BSiMS), though  $\gamma$ -value of the poly(BSnMS) showed still high ( $\gamma=4.9$ ) than common nega-working resists ( $\gamma=1 \sim 3$ ) (15-16)(20-21). Our results obtained in this study showed again the polymers with narrow molecular weight distribution to exhibit higher  $\gamma$ -value than that with broad one.

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19. Maximum yield of BSnMS was obtained under the conditions of  $[\text{MST}]_0 / [\text{DPA}]_0 / [\text{LDA}]_0 / [\text{TMSnCl}]_0 = 0.1 / 0.2 / 0.2 / 0.2$  (mol  $\text{dm}^{-3}$ ), temp 20 °C; time 15.5 h, after TMSnCl was purified severely.
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