# Protection and Polymerization of Functional Monomers. 20. Anionic Polymerizations of 4-Vinylphenyl *tert*-Butyldimethylsilyl Sulfide and 2-(4-Vinylphenyl)ethyl *tert*-Butyldimethylsilyl Sulfide

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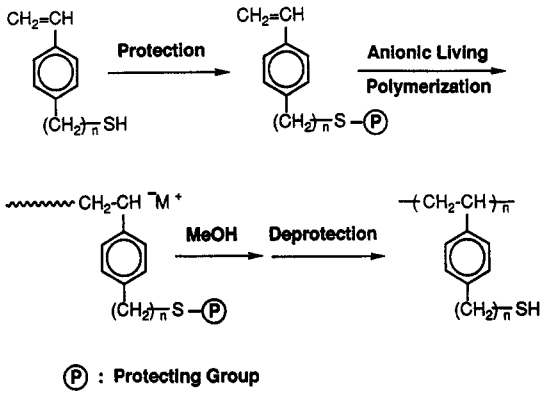
ABSTRACT: The anionic polymerizations of 4-vinylphenyl *tert*-butyldimethylsilyl sulfide (**1a**), (4-vinylphenyl)methyl *tert*-butyldimethylsilyl sulfide (**2a**), and 2-(4-vinylphenyl)ethyl *tert*-butyldimethylsilyl sulfide (**3a**) were carried out in THF at −78 °C. Monomers **1a** and **3a** undergo polymerization with initiators such as butyllithium, metal naphthalenides, and living oligomers of α-methylstyrene. Polymers of **1a** have narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.11–1.13). Their $\bar{M}_n$ values estimated by SEC were proportional to those calculated from [M] to [I] ratios. The absolute $\bar{M}_n$ values could not be measured, since the polymers became insoluble after repeated reprecipitation using THF–methanol, probably with partial cleavage of the S–Si bond, followed by oxidative coupling of the resulting SH groups. Polymers of **3a** were stable and purified by reprecipitation. They had molecular weights predictable from [M] to [I] ratios and the narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.1$). Postpolymerization also indicates that the polymerization of **3a** is living. Complete deprotection of the *tert*-butyldimethylsilyl group from the polymer of **3a** gave quantitatively a soluble linear poly[2-(4-vinylphenyl)ethyl mercaptan]. In marked contrast to **1a** and **3a**, no appreciable polymerization of **2a** was observed under the same conditions.

## Introduction

Synthesis of polymers with well-regulated chain lengths as well as functional groups in all monomer units will be of great interest for the molecular design of polymeric materials. We have begun, since 1982, a research program directed at synthesizing such polymers.[1] For this purpose, we have been developing a new strategy which involves protection and anionic living polymerization of functional monomers, followed by deprotection from the resulting polymers.[2] In fact, a variety of polystyrenes with functional groups (OH, $NH_2$, CHO, COOH, $COCH_3$, and C≡CH) could be successfully synthesized by careful choice of the protecting group and a control of the conditions of anionic living polymerization.[3] These polymers possessed, of course, molecular weights dependent on the [M] to [I] ratios and very narrow molecular weight distributions. Novel block copolymers having these polymer segments could also be made. Thus, this strategy appeared to hold considerable promise for the synthesis of well-defined functional polymers.

We now report the synthesis of well-defined polystyrenes with a pendant mercapto (SH) group by anionic living polymerizations of styrenes with suitably protected SH groups, followed by deprotection as shown in the following scheme:




Many important reactions of SH groups may be considered, such as nucleophilic additions and substitutions, reactions involving thiyl radicals, and oxidation of thiols.[4] Thiols are key starting materials of sulfur compounds and can be transformed into various organosulfur compounds. They are well-known to be important for their roles in metal thiolate chemistry associated with heavy metals such as mercury and lead. Thiols are also important in biological chemistry. Recently, it has been reported that long-chain thiols adsorb from solution onto gold and form densely packed, oriented monolayers.[5] Thus, polymers with SH groups may possibly play an important role as functional polymers in a wide variety of fields.

Because of the high reactivity of the SH group under ionic or radical-forming conditions, difficulties are always encountered in the radical and ionic polymerizations of vinyl monomers with SH groups.[6] To circumvent these difficulties, the SH group must be protected when the polymerizations are to be carried out. Radical-initiated polymerizations of monomers with thiol-protected functionalities were previously reported by several research groups.[7]

Since our aim was the synthesis of polymers with the SH group by anionic living polymerization, we had to use a protecting group for the SH function which would be stable during anionic living polymerization and could be readily and completely removed under mild conditions. Unfortunately, most of the protecting groups are unsatisfactory by the above criterion.[8] For example, although a thioether is stable toward alkyllithium compounds often used as initiators in anionic living polymerization of styrene, its quantitative cleavage is generally difficult even

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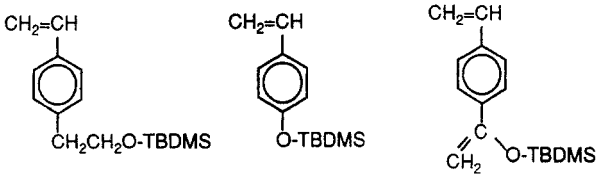
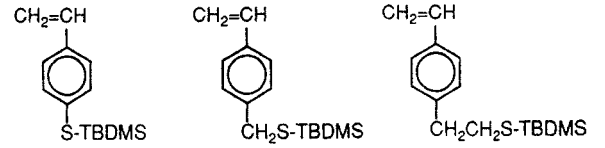
under vigorous conditions. The hemithioacetal and thioacetal protecting groups can be removed by mildly acidic conditions that do not cleave thioethers. They are relatively stable to highly reactive basic reagents, but proton abstraction from methylene groups between S and O (or S) atoms often occurs under similar conditions. Thioesters, thiocarbonates, and thiocarbamates have been used for protection of SH groups in radical polymerization but are not suitable for anionic polymerization because of their lability toward nucleophilic reactions.

We have recently demonstrated that the *tert*-butyldimethylsilyl (TBDMS) group is very effective for the protection of alcohol,[9] phenol,[1,10] and enol[3c] functions of styrene derivatives under anionic living polymerization conditions. This is of particular interest since the less bulky trimethylsilyl group does not protect phenol and enol functions under the same conditions. Stable living polymers are produced from the following styrene derivatives:




On the basis of the effective protection of TBDMS group, we employed the TBDMS group for protection of the thiols of 4-vinylthiophenol and the related monomers during anionic polymerization. The monomers used are 4-vinylphenyl TBDMS sulfide (**1a**), (4-vinylphenyl)methyl TBDMS sulfide (**2a**), and 2-(4-vinylphenyl)ethyl TBDMS sulfide (**3a**). They are the TBDMS ethers of 4-vinylthiophenol (**1**), (4-vinylphenyl)methyl mercaptan (**2**), and 2-(4-vinylphenyl)ethyl mercaptan (**3**), the thiols of which are protected with TBDMS group as shown below:




## Experimental Section

**Materials.** 4-Chlorostyrene and 4-(chloromethyl)styrene were distilled over $CaH_2$ under a reduced pressure. 4-Bromothiophenol TBDMS chloride and *n*- and *sec*-butyllithium (BuLi) were used without purification. Tetrahydrofuran (THF) was refluxed over Na wire and distilled over $LiAlH_4$ under a nitrogen atmosphere and then distilled from its sodium naphthalenide solution on the vacuum line. Cumylpotassium was prepared from cumyl methyl ether and an excess amount of Na–K alloy in THF. Similarly, Li and K naphthalenides were prepared from naphthalene and Li and K, respectively. Living oligomers of $\alpha$-methylstyrenes were always prepared just prior to the polymerization from BuLi, Li and K naphthalenides, and $\alpha$-methylstyrene in THF. $LiAlEt_4$ was prepared from Li and $Et_3Al$ according to the previous method.[11]

**Monomers.** The TBDMS-protected monomers (**1a–3a**) were prepared as described later and were purified by fractional distillation over $CaH_2$ under a nitrogen atmosphere. These monomers were distilled over $CaH_2$, phenylmagnesium chloride, and $LiAlEt_4$ (3–5 mol %) on the vacuum line into the ampoules with breakseals.

**4-Bromophenyl TBDMS sulfide** was prepared by the reaction of sodium 4-bromothiophenoxide (76.8 mmol) with TBDMS chloride (15.7 g, 105 mol) in THF. After usual workup, the resulting mixture was fractionally distilled at 93–94 °C (1 mmHg), affording 18.3 g (79%) of 4-bromophenyl TBDMS sulfide as a colorless oil: 90-MHz $^1$H NMR ($CDCl_3$) $\delta$ 0.17 (6H, s, $SiCH_3$), 0.91 (6H, s, $SiCCH_3$), 7.11–7.42 (4H, m, Ar).

**4-Vinylphenyl TBDMS Sulfide (1a).** A solution of 4-bromophenyl TBDMS sulfide (18.3 g, 60.4 mmol) in dry ether (40 mL) was added dropwise to a refluxing mixture of Mg (4.03 g, 166 mmol) in dry ether (20 mL) under a nitrogen atmosphere. The solution was refluxed for an additional 2 h and cooled to 0 °C. To this was added $NiCl_2(Ph_2PCH_2CH_2PPh_2)$ (0.32 g, 0.59 mol) under a nitrogen atmosphere. To this mixture was added dropwise 12.1 g (113 mmol) of vinyl bromide in dry ether (30 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and at 25 °C for 3 h. After usual workup, the remaining oil was fractionally distilled at 76–77 °C (2 mmHg) to give 9.53 g (47%) of **1a** as a colorless liquid: 90-MHz $^1$H NMR ($CDCl_3$) $\delta$ 0.18 (6H, s, $SiCH_3$), 0.97 (9H, s, $SiCCH_3$), 5.24, 5.72 (2H, 2d, $J$ = 10.8, 17.6 Hz, $CH_2$=), 6.68 (1H, dd, CH=), 7.18–7.44 (4H, m, Ar); 22.5-MHz $^{13}$C NMR ($CDCl_3$) $\delta$ −3.1 ($SiCH_3$), 19.1 ($SiCCH_3$), 26.5 ($SiCCH_3$), 114.0 (=$CH_2$), 126.5 (Ar, C2, C3), 131.2 (Ar, C1), 135.7 (CH=), 136.3 (Ar, C4); IR (KBr) 1629, 1250, 990, 905, 803, 771 cm$^{-1}$. Anal. Calcd for $C_{14}H_{22}SSi$: C, 67.12; H, 8.87; S, 12.80. Found: C, 67.06; H, 9.12; S, 12.98.

**(4-Vinylphenyl)methyl Mercaptan (2).** **2** was prepared from 4-(chloromethyl)styrene (20.9 g, 137 mmol), thiourea (13.3 g, 175 mmol), and ethanol (100 mL) at reflux for 3 h. The residue was precipitated by adding a large excess of diethyl ether. Recrystallization from acetone–methanol (10/1 v/v) gave the pure *s*-isothiouronium salt as a white solid (22.4 g, 72%). The salt was treated with 2 N NaOH to give a crude **2** (>95% purity by GC), which was used without purification. All operations were carried out using nitrogen-bubbled solvents under a nitrogen atmosphere: 90-MHz $^1$H NMR ($CDCl_3$) $\delta$ 1.74 (1H, t, $J$ = 7.5 Hz, SH), 3.72 (2H, d, Ph$CH_2$S), 5.22, 5.71 (2H, 2 d, $J$ = 10.8, 17.6 Hz, $CH_2$=), 6.70 (1H, dd, CH=), 7.20–7.42 (4H, m, Ar).

**(4-Vinylphenyl)methyl TBDMS sulfide (2a).** **2a** was prepared by the reaction of sodium (4-vinylphenyl)methyl mercaptide (33.5 mmol) with TBDMS chloride (6.03 g, 40.2 mmol) in dry THF. After the usual workup, the resulting yellow oil was distilled at 121–3 °C (0.7 mmHg), affording 5.75 g (65%) of **2a** as a colorless oil: 90–MHz $^1$H NMR ($CDCl_3$) $\delta$ 0.26 (6H, s, $SiCH_3$), 0.97 (9H, s, $SiCCH_3$), 3.71 (2H, s, $SCH_2$), 5.21 5.70 (2H, 2 d, $J$ = 10.8, 17.6 Hz, $CH_2$=), 6.70 (1H, dd, CH=), 7.31 (4H, m, Ar); 22.5-MHz $^{13}$C NMR ($CDCl_3$) $\delta$ −3.4 ($SiCH_3$), 19.1 ($SiCCH_3$), 26.5 ($SiCCH_3$), 30.5 ($CH_2S$), 113.6 (=$CH_2$), 126.4 (Ar, C2), 128.7 (Ar, C3), 136.3 (Ar, C1), 136.7 (CH=), 140.4 (Ar, C4); IR (KBr) 1629, 1250, 990, 905, 803, 771 cm$^{-1}$. Anal. Calcd for $C_{15}H_{24}SSi$: C, 68.98; H, 9.43; S, 11.51. Found: C, 68.47; H, 9.96; S, 10.92.

**[2-(4-Vinylphenyl)ethyl]isothiouronium bromide** was prepared from 4-(2-bromoethyl)styrene[12] (28.3 g, 134 mmol) and thiourea (10.7 g, 141 mmol) in ethanol. Recrystallization from acetone gave the *s*-isothiouronium salt as a white solid (24.0 g, 73%): 90-MHz $^1$H NMR ($D_2O$ at 65 °C) [$(CH_3)_3Si(CH_2)_3SO_3Na$ was used as a standard ($\delta$ = 0.015 ppm)] $\delta$ 3.07 (2H, t, $CH_2S$), 3.44 (2H, t, $CH_2CS$), 4.40 (4H, br s, $NH_2$ and =$NH_2^+$), 5.34, 5.85 (2H, 2 d, $J$ = 10.7, 17.8 Hz, CH=), 6.83 (1H, dd, $CH_2$=), 7.41 (4H, m, Ar).

**2-(4-Vinylphenyl)ethyl mercaptan (3)** was obtained by the hydrolysis of [2-(4-vinylphenyl)ethyl]isothiouronium bromide with 2 N NaOH. After usual workup, crude **3** (>95% purity) was obtained as a pale yellow oil (86% yield): 90-MHz $^1$H NMR ($CDCl_3$) $\delta$ 2.85 (4H, m, $SCH_2CH_2$), 5.21, 5.72 (2H, 2 d, $J$ = 11.7, 17.1 Hz, $CH_2$=), 6.71 (1H, dd, CH=), 7.29 (4H, m, Ar).

**2-(4-Vinylphenyl)ethyl TBDMS Sulfide (3a).** **3a** was prepared in a similar manner of **2a** from sodium 2-(4-vinylphenyl)-ethyl mercaptide and TBDMS chloride in 57% yield: 90-MHz $^1$H NMR ($CDCl_3$) $\delta$ 0.25 (6H, s, $SiCH_3$), 0.95 (9H, s, $SiCCH_3$), 2.77–2.81 (4H, m, $SCH_2CH_2$), 5.20, 5.69 (2H, 2 d, $J$ = 10.8, 16.5 Hz, $CH_2$=), 6.68 (1H, dd, CH=), 7.24 (4H, m, Ar); 22.5-MHz $^{13}$C NMR ($CDCl_3$) $\delta$ −3.5 ($SiCH_3$), 19.1 ($SiCCH_3$), 26.4 ($SiCCH_3$), 28.0 ($SCH_2CH_2$), 39.6 ($CH_2S$), 113.3 (=$CH_2$), 126.4 (Ar, C2), 128.7 (Ar, C3), 135.9 (Ar, C1), 136.7 (CH=), 140.5 (Ar, C4); IR (KBr) 1629, 1248, 990, 905, 803, 769 cm$^{-1}$. Anal. Calcd for $C_{16}H_{28}SSi$: C, 69.12; H, 9.36; S, 11.54. Found: C, 69.42; H, 9.55; S, 11.78.

**Deprotection of the TBDMS Group from Poly(3a).** Acid hydrolysis of the TBDMS group from poly(**3a**) was carried out under nitrogen using the nitrogen-bubbled (30 min) solvents. A typical experiment was as follows: A solution of poly(**3a**) ($\bar{M}_n$ =

26 000, 0.190 g, 0.67 mmol, calculated as a monomer unit) in 1,4-dioxane (19 mL) was added to a solution of HCl (3 mL) in 1,4-dioxane (19 mL) at 25 °C, and the mixture was allowed to stir for a few hours. The polymer was then directly freeze-dried from the reaction mixture to remove HCl, $H_2O$, and 1,4-dioxane. The polymer thus isolated was carefully reprecipitated twice from THF solution to methanol under a nitrogen atmosphere and freeze-dried from the benzene solution. A benzene-soluble polymer (0.110 g) was obtained. It was identified to be poly[2-(4-vinylphenyl)ethyl mercaptan] by the $^1H$ and $^{13}C$ NMR and IR spectra: 90-MHz $^1H$ NMR ($CDCl_3$) $\delta$ 0.6–2.0 (4H, m, $CH_2CH$ and SH), 3.2 (4H, m, $CH_2CH_2S$), 6.0–7.2 (4H, m, Ar); IR (KBr) 2563 $cm^{-1}$ (S-H stretching). Anal. Calcd for $(C_{16}H_{27}S)_n$: C, 76.8; H, 10.8; S, 12.4. Found: C, 76.9; H, 10.0; S, 12.7. Similarly, the TBDMS groups were deprotected to regenerate SH functions from the block copolymers.

**Measurements.** IR spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrometer. $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL FX-90Q (89.6-MHz $^1H$ and 22.53-MHz $^{13}C$) in $CDCl_3$. Chemical shifts were reported in ppm downfield relative to $(CH_3)_4Si$ ($\delta$ 0) for $^1H$ NMR and $CDCl_3$ ($\delta$ 77.1) for $^{13}C$ NMR spectra as standards. Size-exclusion chromatograms (SEC) were obtained at 40 °C with a Toyo Soda HLC-8020 instrument with ultraviolet (254 nm) or refractive index detection. THF was the carrier solvent at a flow rate of 0.8 mL/min. For determination of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values, three polystyrene gel columns (TOSOH G5000$H_{LX}$, G4000$H_{LX}$, and G3000$H_{LX}$) were used. Vapor pressure osmometry (VPO) for absolute $\bar{M}_n$ determinations was made with a Corona 117 instrument in benzene solution with a highly sensitive thermoelectric couple and equipment. The values of $\bar{M}_n$ were determined within analytical error of ±5% in the $\bar{M}_n$ range from $10^2$ to $10^5$.

## Results and Discussion

Before attempting the anionic polymerizations of **1a**–**3a**, we checked that the $^t$BuMe$_2$Si–S bond is stable toward the living polystyryl anions because the Me$_3$Si–S bond of phenyl trimethylsilyl sulfide is reported to be unstable in the presence of the organolithium compound.[13]

A 10-fold excess of phenyl TBDMS sulfide as a monomer model compound of **1a** was added at −78 °C to either polystyryllithium or polystyrylpotassium, and the mixture was allowed to stand at −78 °C for 24 h. Then, the red-colored polystyryl anions were titrated to the colorless endpoint by 1-octanol in a sealed reactor under high vacuum. The results indicated no loss of either carbanions under these conditions. This suggests that the $^t$BuMe$_2$S–Si bond is stable toward the living polystyryl anions. Accordingly, the monomer **1a** and the related monomers, **2a** and **3a**, would be expected to undergo living polymerization, similar to that of styrene.

**Synthesis of Monomers.** The synthesis of vinylthiophenol (**1**) is often difficult because of addition of the SH group across the double bond. Under careful conditions, **1** was generally synthesized by dehydration of 4-(1-hydroxyethyl)thiophenol over $Al_2O_3$ at 300 °C.[14] The yield of **1** reported by this method was low from the starting 4-aminophenyl methyl ketone. We attempted to synthesize **1** by the reaction of the Grignard reagent of 4-vinylphenyl chloride with sulfur, followed by $LiAlH_4$ reduction. The crude yield of **1** was good in this reaction. Again, the yield was considerably reduced by the distillation, probably due to the addition reaction referred to above.

To circumvent these difficulties, we protected the SH group with a TBDMS group prior to the introduction of the double bond. 4-Bromothiophenol was treated with NaH and silylated with TBDMS chloride. The silylated thiophenol was converted into the Grignard reagent which reacted directly with vinyl bromide in the presence of a catalytic amount of $NiCl_2$–(1,2-bis(phenylphospho)ethane complex.[15] As much as 60–85% of crude **1a** (40% after purification) was obtained from the starting 4-bromothiophenol. Thus, **1a** was successfully synthesized in moderate yields.

For the synthesis of (4-vinylphenyl)methyl mercaptan (**2**), we employed two routes which include the reaction of the Grignard reagent of 4-vinylbenzyl chloride with sulfur, followed by reduction with $LiAlH_4$, and the reaction of 4-vinylbenzyl chloride with thiourea to give the corresponding isothiouronium salt and hydrolysis of the latter.[16] The first reaction using the Grignard reagent gave an unexpectedly low yield of **2**. We were unable to increase the efficiency of this reaction. On the other hand, the formation of isothiouronium salt and its hydrolysis products was found to proceed more efficiently, affording **2** in 60% yield.

There are various methods by which a thiol can be protected by silyl groups. Among them, the reaction of the sodium salt of **2** with TBDMS chloride gave the best yield of **2a** in our hands. Under nitrogen, treatment of **2** with a slight excess of sodium hydride in THF at 0 °C afforded the corresponding sodium mercaptide which was allowed to react with TBDMS chloride in THF to give the silyl-protected monomer, **2a**, in 65% yields even after purification.

Similarly, 2-(4-vinylphenyl)ethyl mercaptan (**3**) was prepared in 62% yield from 2-(4-vinylphenyl)ethyl bromide to the isothiouronium salt and then hydrolysis. **3** was treated with sodium hydride, followed the TBDMS chloride, to afford **3a** in 57% yield.

**Anionic Polymerizations of 1a.** As reported in our previous papers,[1,3c,9,10] **1a** was purified by distillation first over finely powdered $CaH_2$ and then phenylmagnesium chloride on a vacuum line. The anionic polymerization of **1a** was carried out in THF at −78 °C to avoid possible side reactions, especially the attack of carbanionic species on the S–Si bond of **1a**. The initiators used were *n*-BuLi, potassium naphthalenide, and a potassium salt of living oligo($\alpha$-methylstyrene).

Upon addition of **1a** into each of the initiator solutions, the characteristic orange-red or dark red color of the styryl anion produced from **1a** appeared. These colors remained unchanged at −78 °C for at least 30 min. Termination was accomplished by addition of a few drops of degassed methanol, and the color disappeared immediately. The polymerizations were completed even after 5 min as evidenced by the GC analysis that no monomers remained. The polymerization mixtures were then poured into an excess of methanol to precipitate the polymers.

Unfortunately, the polymer from **1a** always became insoluble during the repeated reprecipitation from THF solution to MeOH. Even after the first reprecipitation, a high molecular weight shoulder was observed in the SEC trace. After twice reprecipitation, a significant amount of the THF-insoluble part was produced and the SEC trace became multimodal in a THF-soluble fraction. Finally, the polymer became insoluble after several reprecipitations. This may be due to the partial undesirable cleavage of the S–SiMe$_2$Bu$^t$ bond, followed by the oxidative S–S bond formation between intermolecular polymer SH side chains leading to cross-linking. Therefore, the polymer was carefully precipitated in nitrogen-bubbled methanol under an atmosphere of nitrogen and was analyzed directly by SEC without further purification.

$^1H$ and $^{13}C$ NMR studies of the polymer thus obtained were entirely consistent with the expected polymer structure. The SEC analysis showed that the polymers all possessed symmetrical unimodal peaks with the relatively

Table 1. Anionic Polymerization of 1a in THF at −78 °C for 0.5 h[a]

| monomer | initiator | | α-MeSt,[b] | $10^{-3}\bar{M}_n$ | | |
|---|---|---|---|---|---|---|
| 1a, mmol | type | mmol | mmol | calcd | obsd[c] | $\bar{M}_w/\bar{M}_n$[d] |
| 2.04 | BuLi[e] | 0.0698 | 0.250 | 7.7 | 5.5 | 1.12 |
| 2.11 | K-Nap[f] | 0.0867 | 0.300 | 13 | 7.1 | 1.11 |
| 2.23 | K-Nap | 0.0522 | 0.319 | 23 | 14 | 1.13 |

[a] Yields of polymers were quantitative. [b] α-Methylstyrene. [c] $\bar{M}_n$ (obsd) was estimated by SEC curve by using the calibration of standard polystyrene. [d] $\bar{M}_w/\bar{M}_n$ was determined from SEC curve by using the calibration of standard polystyrene. [e] n-Butyllithium. [f] Potassium naphthalenide.

broad molecular weight distributions in the $\bar{M}_w/\bar{M}_n$ range of 1.3–1.7. Their $\bar{M}_n$ values were in the range of 10 000–30 000 that were estimates relative to polystyrene standards. The molecular weight distribution of the resulting polymer is narrowed considerably by using the more purified **1a** which is obtained on the vacuum line by the distillations over $CaH_2$, $C_6H_5MgCl$, and finally $LiAlEt_4$. The polymers with $\bar{M}_w/\bar{M}_n$ values of 1.11–1.13 were obtained as shown in Table 1. In these cases, sharp and unimodal peaks were observed in their SEC charts, but small high molecular weight shoulders again appeared in the samples which were allowed to stand for long time or purified by reprecipitation even under careful conditions. It can be seen from the table that the $M_n$ values estimated by their SEC curves are proportioned to those calculated from [M] to [I] ratios, although the former's are again always smaller than the latter.

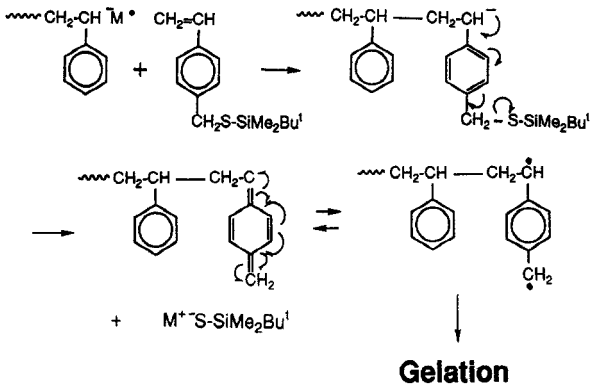
Further purification and characterization of the resulting polymers were precluded by their instability. The results estimated by SEC and the appearance of the characteristic red color in the polymerizing system indicate the living character of the polymerization of **1a**. It can be concluded that the TBDMS group protects satisfactorily the SH function during the polymerization. Furthermore, it was found that the TBDMS group was readily and completely deprotected from the resulting poly(**1a**) under mild conditions.[17] These characteristics of the TBDMS group are advantageous for both protecting the SH function of **1a** during the polymerization and regenerating the SH function.

Unfortunately, a difficulty was encountered for further purification of the poly(**1a**) due to the cleavage of $^tBuMe_2$-Si–S bond during reprecipitation workup. We could not purify the polymer sufficiently to measure the absolute $\bar{M}_n$ value. Even by several careful SEC analyses of the polymers, we could not obtain a unimodal peak without small high molecular weight shoulders which might arise from the coupling between polymer chains after isolation. Thus, a direct and definite proof is not available at the present time for the living character of the polymerization of **1a**. Use of a more stable protective group or direct transformation from S–$SiMe_2Bu^t$ to a more stable bond is required to prove the living character of the polymerization.

**Anionic Polymerization of 2a.** The anionic polymerization of **2a** was carried out in THF with either Li or K naphthalenides, or oligo(α-methylstyryl)dipotassium at −78 °C for 0.5–1 h. When the monomer in THF solution was added to the initiator, the characteristic green or dark red color disappeared immediately. No polymer was obtained, and unreacted **2a** was recovered nearly quantitatively.

We first attributed the inability of **2a** to polymerize to the benzylic proton abstraction of **2a** by either the initiator or the growing active chain end, if produced. An attack by these carbanions on silicon is also considered as a possible side reaction. Both of these possibilities can be ruled out since gelation occurs immediately by the reaction of **2a** with polystyrylpotassium. If the above-mentioned reactions could take place, a soluble polystyrene terminated by the protonation or the silylation of polystyrylpotassium would be produced instead of the gel. The IR spectrum showed that the gelatinous material consisted mostly of polystyrene, which is probably cross-linked polystyrene, since it is insoluble in organic solvents. However, most of the starting **2a** was recovered.

We therefore consider a more likely mechanism to explain the observations, i.e., no polymerization of **2a** and gelation caused by the reaction of living polystyrene with **2a**. The carbanion at the polymer chain end may induce 1,6-elimination to generate the very reactive *p*-xylylene intermediate, which reacts readily by radical combination to form a cross-linked polymer network. Some suggestive observations and the reaction mechanism producing xylylene intermediate were previously reported by Rickborn and his co-workers.[18] Thus, this mechanism can




explain the polymerization results with **2a**. However, more direct evidence is needed to characterize a reaction pathway for **2a** which is now under investigation. We have recently found very similar observations in the anionic polymerizations of the structurally similar oxygen-containing styrene derivatives such as the TBDMS ether of (4-vinylphenyl)methanol[19] and 2-(4-vinylphenyl)-1,3-dioxolane.[3a] Neither monomer polymerized. Polystyrene gel formation and nearly quantitative recovery of the monomers were observed in the reactions of living polystyrene with both monomers. Since the structural skeletons of these monomers and **2a** are the same, they bear the benzyl ether and thioether linkages, which may possibly lead to the elimination reaction referred to above.

**Anionic Polymerization of 3a.** **3a** was purified on the vacuum line by distillation over finely granular $CaH_2$, phenyl chloride-free $C_6H_5MgCl$, and finally $LiAlEt_4$.[20] The **3a** thus purified was employed in the anionic polymerization with the following initiators: *n*-BuLi, *s*-BuLi, oligo(α-methylstyryl)lithium and -dilithium, cumylpotassium, potassium naphthalenide, and oligo(α-methylstyryl)dipotassium.

When **3a** in THF was added to each of the initiator solutions, the reaction mixtures exhibited an orange-red color with $Li^+$ and a dark red color with $K^+$, respectively. Appearance of the colors is characteristic of styryl anions. The colors remained unchanged at −78 °C after 24 h, indicating that the polystyryl anions are stable. After the polymerizations for 5–30 min, termination was accomplished with degassed methanol and the colors disappeared immediately. GC analysis indicated that the polymerization of **3a** was completed in 5 min.

The polymers were obtained quantitatively and purified thrice by reprecipitation from THF to methanol. They

Table 2. Anionic Polymerization of 3a in THF at −78 °C for 0.5 h[a]

| monomer | initiator | | α-MeSt,[b] | $10^{-3}\bar{M}_n$ | | |
|---|---|---|---|---|---|---|
| 3a, mmol | type | mmol | mmol | calcd | obsd[c] | $\bar{M}_w/\bar{M}_n$[d] |
| 2.80 | BuLi[e] | 0.0818 | – | 9.5 | 9.7 | 1.09 |
| 2.04 | BuLi | 0.0442 | – | 13 | 13 | 1.08 |
| 2.61 | BuLi | 0.0392 | – | 19 | 19 | 1.05 |
| 5.34 | BuLi | 0.0283 | – | 53 | 67 | 1.03 |
| 2.08 | s-BuLi[f] | 0.0714 | – | 8.1 | 11 | 1.05 |
| 1.94 | BuLi | 0.0535 | 0.303 | 11 | 13 | 1.04 |
| 2.20 | Li-Nap[g] | 0.113 | 0.310 | 11 | 12 | 1.07 |
| 1.96 | cumylK[h] | 0.0673 | – | 8.1 | 8.2 | 1.23 |
| 1.81 | K-Nap[i] | 0.113 | 0.318 | 8.9 | 9.0 | 1.19 |
| 1.68 | K-Nap | 0.0788 | 0.318 | 13 | 11 | 1.34 |
| 1.89 | K-Nap | 0.0861 | – | 13 | 14 | 1.19 |

[a] Yields of polymers were quantitative. [b] α-Methylstyrene. [c] $\bar{M}_n$ (obsd) was obtained by VPO in benzene solution. [d] $\bar{M}_w/\bar{M}_n$ was determined from SEC curve by using the calibration of standard polystyrene. [e] n-Butyllithium. [f] sec-Butyllithium. [g] Lithium naphthalenide. [h] Cumylpotassium. [i] Potassium naphthalenide.

are definitely stable to the purification workup in air, and no special care is needed for their handling. Thus, the $^t$BuMe$_2$Si–S bond of poly(**3a**) is apparently stable compared to that of poly(**1a**) which is gradually cleaved under the same conditions.

The IR spectrum showed characteristic absorptions at 485, 769, 803, and 1248 cm$^{-1}$ which corresponded to S–Si and Si–CH$_3$ bonds, respectively. The $^1$H NMR spectrum showed two characteristic sharp resonances for the methylsilyl at 0.25 ppm and methyl protons at 0.95 ppm and broad resonances assigned to the phenyl at 6–7 ppm and the main-chain methylene and methine protons at 0.5–2 ppm. Resonances for the CH$_2$CH$_2$ group between the phenyl and silyl groups appeared at the same chemical shift of 2.70 ppm. Thus, chemical shifts and integral ratios for all the resonances indicate that vinyl polymerization occurs exclusively. The reasonable integral ratio of phenyl and CH$_3$–Si protons also indicates no cleavage of the $^t$BuMe$_2$Si–S bond. The $^{13}$C NMR spectrum was observed to be consistent with the assigned structure by $^1$H NMR. Since the poly(**3a**) is stable in air, the direct characterizations by SEC and VPO is possible in this protected form. The results are summarized in Table 2.

The SEC curves showed that the molecular weight distributions were very narrow in all polymers obtained with the organolithium initiators such as BuLi, s-BuLi, and oligo(α-methylstyryl)lithium prepared from BuLi and α-methylstyrene. A difunctional initiator prepared from lithium naphthalenide and α-methylstyrene also works well, with $\bar{M}_w/\bar{M}_n$ values less than 1.1. It can be seen from Table 2 that there is good agreement between the observed and calculated molecular weights from [M] and [I] ratios. These results demonstrate the living character of the polymerization of **3a** under these conditions. Appearance of the characteristic red color in the polymerizing systems also strongly shows that the polymerization is living.

On the other hand, somewhat broad distributions of molecular weight were observed in polymers obtained with the initiators such as potassium naphthalenide, cumylpotassium, and oligo(α-methylstyryl)dipotassium. Their $\bar{M}_w/\bar{M}_n$ values were in the range of 1.19 and 1.34. The molecular weights calculated and observed in all samples are identical within experimental accuracy (Table 2). We therefore believe that **3a** undergoes living polymerization when initiated with organopotassium compounds. The broadened distribution may possibly be explained by rapid propagation relative to the initiation. Thus, the TBDMS group satisfactorily protects the SH function of **3** for anionic living polymerization.

Table 3. Block Copolymerization of 3a with Styrene at −78 °C in THF with n-Butyllithium[a]

| type of block copolymer | A monomer | B monomer | block copolymer[b] $10^{-3}\bar{M}_n$ (calcd) | $10^{-3}\bar{M}_n$ (obsd)[c] | $\bar{M}_w/\bar{M}_n$[d] |
|---|---|---|---|---|---|
| A–B[e] | **3a** | styrene | 18 | 21 | 1.07 |
| B–A[f] | **3a** | styrene | 19 | 20 | 1.06 |

[a] Yields of polymers were quantitative. [b] Polymerization times at the first and at the second stages were both 0.5 h. [c] $\bar{M}_n$ (obsd) was obtained by VPO in benzene solution. [d] $\bar{M}_w/\bar{M}_n$ was determined from SEC curve by using the calibration of standard polystyrene. The amounts of BuLi, **3a**, and styrene were 0.0641, 1.83, and 6.01 mmol, respectively. [e] $\bar{M}_n$s (calcd) were 8000 and 10 000 for poly(**3a**) and polystyrene segments, respectively. [f] The amounts of BuLi, **3a**, and styrene were 0.0579, 2.21, and 4.38 mmol, respectively. $\bar{M}_n$s (calcd) were 11 000 and 7900 for poly(**3a**) and polystyrene segments, respectively.

**Block Copolymerization of 3a and Styrene.** One of the benefits provided by living polymerization includes the synthesis of well-defined block copolymers. Such block copolymers can be used as proof for the stability and reactivity of the active growing chain end obtained by the first-stage living polymerization.

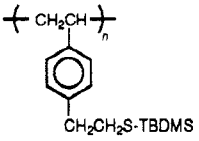
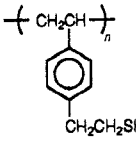
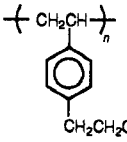
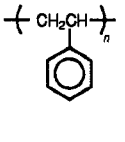
At first, the block copolymerization was carried out by the sequential addition of **3a** and styrene with BuLi in THF at −78 °C. The polymer was obtained quantitatively. The SEC curve showed that the polymer possessed a symmetrical unimodal peak with a narrow distribution with $\bar{M}_w/\bar{M}_n$ value of 1.07. The composition of both segments observed by $^1$H NMR was consistent with that calculated from the monomer ratios in the feed. The agreement of the $\bar{M}_n$ value calculated and observed by VPO is shown in Table 3. These indicate clearly that the block copolymerization proceeds as expected. The fact that the carbanion of growing chain end derived from **3a** is stable and can polymerize styrene also provides direct evidence for the living character of the polymerization of **3a**.

A reverse addition of monomers with styrene added first also produced a desired block copolymer with the predictable $\bar{M}_n$ and composition and a narrow molecular weight distribution, as shown in Table 3. Accordingly, the combination of **3a** and styrene is possible for reversible block copolymerization where both blocks can initiate the other with quantitative initiation efficiency. This suggests that the reactivities of **3a** and the living polymer from **3a** are nearly equal to those of styrene monomer and the living polystyrylanion, respectively.

**Deprotection of the TBDMS Group To Regenerate the SH Group from Poly(3a).** Since it is well-known that thiols are not stable and readily oxidized even by oxygen in the air, the experiment of deprotection is carefully carried out in degassed and nitrogen-saturation solvents under an atmosphere of nitrogen. The TBDMS group from the poly(**3a**) was successfully deprotected with 0.9 N HCl in 1,4-dioxane–H$_2$O (13/1, v/v) at 25 °C for a few hours.

The absorptions for S–Si and Si–CH$_3$ bonds at 485, 769, 803, and 1248 cm$^{-1}$ disappeared in the IR spectrum of the resulting polymer thus obtained. Instead, the absorption at 2563 cm$^{-1}$ to SH stretching vibration newly appeared. The $^1$H NMR spectra of the polymers before and after deprotection are shown in Figure 1. They exhibited that two singlets at 0.95 and 0.25 ppm corresponding to C–CH$_3$ and Si–CH$_3$ disappeared completely and a new peak at 1.3 ppm corresponding to the SH proton appeared after deprotection. These results strongly indicate that the TBDMS group is completely deprotected. Evidence for

**Table 4. Solubilities of Poly(3a), Poly(3), Poly[2-(4-vinylphenyl)ethanol], and Polystyrene[a]**

| |  |  |  |  |
|---|---|---|---|---|
| | $CH_2CH_2S$-TBDMS | $CH_2CH_2SH$ | $CH_2CH_2OH$ | |
| hexane | S | I | I | I |
| benzene | S | S | I | S |
| $CCl_4$ | S | swelling | I | S |
| $CHCl_3$ | S | S | I | S |
| acetone | swelling | swelling | I | S |
| diethyl ether | S | I | I | S |
| 1,4-dioxane | S | S | S | S |
| THF | S | S | I | S |
| pyridine | S | S | S | S |
| DMF | S | S | S | S |
| ethanol | I | I | S | I |
| methanol | I | I | S | I |
| water | I | I | I | I |

[a] I, insoluble; S, soluble.

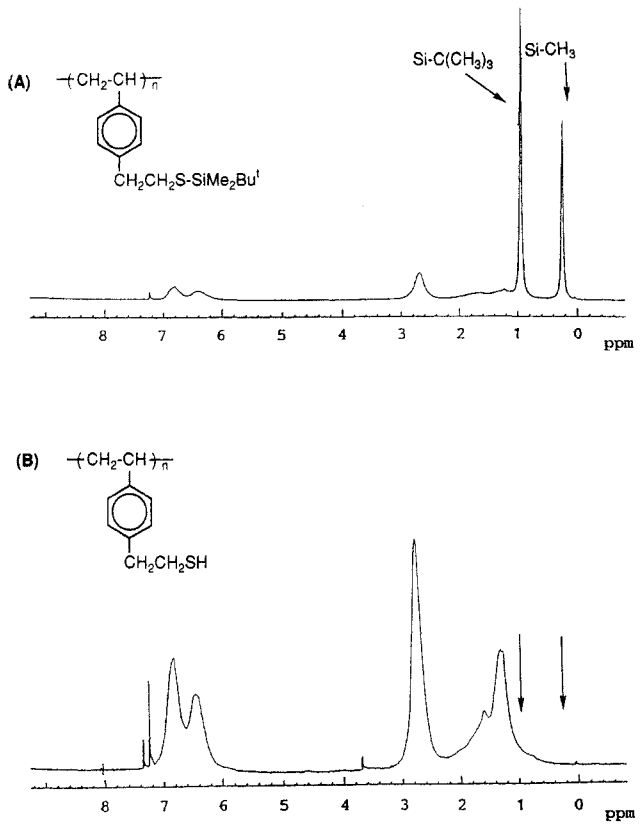



**Figure 1.** $^1H$ NMR spectra of (A) poly(**3a**) and (B) poly[2-(4-vinylphenyl)ethyl mercaptan].

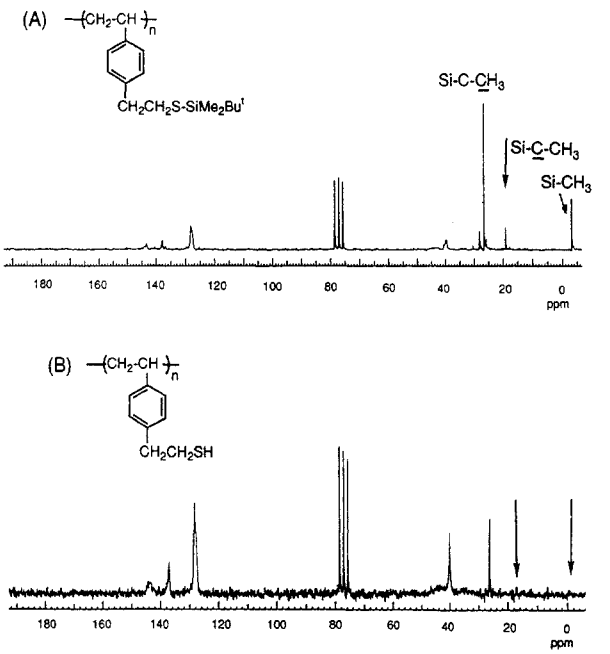



**Figure 2.** $^{13}C$ NMR spectra of (A) poly(**3a**) and (B) poly[2-(4-vinylphenyl)ethyl mercaptan].

complete deprotection was also obtained by the analysis of $^{13}C$ NMR as shown in Figure 2. The poly[2-(4-vinylphenyl)ethyl mercaptan] thus obtained was observed to be stable at least for a few weeks under nitrogen but became insoluble soon in air, possibly due to a cross-linking between intermolecules by the S–S formation.

The solubility of poly(**3**) was examined and listed in Table 4 where the solubilities of poly(**3a**), poly[2-(4-vinylphenyl)ethanol], and polystyrene were added for comparison. The comparison of the solubilities of poly(**3**) with poly[2-(4-vinylphenyl)ethanol] is of particularly interest. The former SH-containing polymer was soluble in benzene, chloroform, and THF but insoluble in methanol and ethanol, while the latter OH-containing polymer showed just the opposite solubilities in these solvents. This clearly indicates that the thiol does not form a stronger hydrogen bond than the corresponding alcohol does.[21]

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(17) Deprotection of the TBDMS group from the poly(**1a**) was readily and completely performed under mild conditions (1 N HCl in a 1,4-dioxane–$H_2O$ mixture (11/1, v/v) at 25 °C for 3 h). The resulting polymer was identified to be poly(4-vinylthiophenol) by IR, $^1H$ NMR, and elemental analysis. However, the poly(4-vinylthiophenol) was not stable and readily became insoluble even under an atmosphere of nitrogen.

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(20) For use of **3a** in the anionic living polymerization, we first attempted to purify **3a** on the vacuum line by distillation in the presence of either $C_6H_5MgCl$ or $C_6H_5CH_2MgCl$. The polymerization of the **3a** thus purified with BuLi proceeded to give a polymer quantitatively. A comparison of the three molecular weights for each polymer showed that the observed $\bar{M}_n$ values were always higher than those calculated, although their molecular weight distributions were found to be narrow. See: $\bar{M}_n$ calcd = 7800, 8100, 14 000. $\bar{M}_n$ obsd = 11 000, 13 000, 27 000. $\bar{M}_w/\bar{M}_n$ = 1.07, 1.05, 1.04. This may indicate destruction of some initiator by impurities prior to polymerization. Therefore, we purified **3a** on the vacuum line by repeated distillations over $CaH_2$ first, $C_6H_5MgCl$, and finally $LiAlEt_4$. The purification of **3a** by this method was effective as indicated by the good agreement between $M_n$ values observed and calculated and the narrow molecular weight distributions as shown in Table 2.

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