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Protection and Polymerization of Functional Monomers. 18. Syntheses of Well-Defined Poly(vinylphenol), Poly[(vinylphenyl)methanol], and Poly[2-(vinylphenyl)ethanol] by Means of Anionic Living Polymerization of Styrene Derivatives Containing *tert*-Butyldimethylsilyl Ethers

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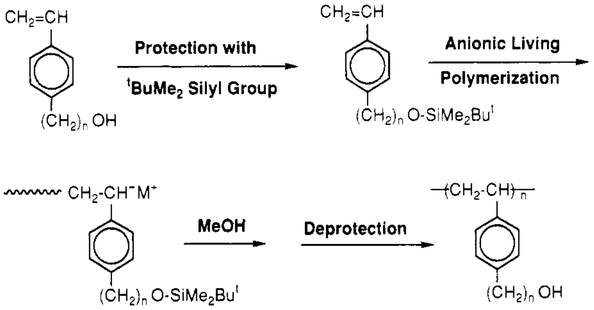
ABSTRACT: Anionic polymerization behaviors of nine styrene derivatives with hydroxy functions protected with *tert*-butyldimethylsilyl groups, e.g., *tert*-butyldimethylsilyl ethers of 4-vinylphenol (**1a**), (4-vinylphenyl)methanol (**2a**), 2-(4-vinylphenyl)ethanol (**3a**), and their meta (**1b**–**3b**) and ortho isomers (**1c**–**3c**), have been examined with various anionic initiators in THF at −78 °C. Among them, **1a**,**b**, **2b**, and **3a**–**c** undergo anionic polymerization without chain-transfer and termination reactions to afford stable living polymers. The resulting polymers all are found to possess molecular weights predictable from [monomer] to [initiator] ratios and narrow molecular weight distributions, the values of $\bar{M}_w/\bar{M}_n$ being around 1.1. Deprotection of the silyl groups from these polymers provides well-defined linear polystyrenes with either phenolic or alcoholic hydroxy groups. As expected, they are shown to retain desirable characteristics of their parent living polymers, e.g., controllable molecular weights and narrow molecular weight distributions. By contrast, attempts to polymerize the structurally analogous **1c**, **2a**, and **2c** have failed. No appreciable polymerization occurs with these monomers under the identical conditions used in the successful polymerizations. The mechanisms for side reactions in the unsuccessful polymerizations are proposed.

Introduction

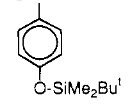
Living polymerization provides an important route to synthesize polymers with well-regulated uniform chain lengths as well as block copolymers with well-defined structures. Although several new living polymerization systems have been recently developed, from a synthetic viewpoint anionic living polymerization of conjugated hydrocarbon monomers such as styrene, 1,3-butadiene, and isoprene is still the best method established to synthesize the above-mentioned homopolymers and block copolymers. Unfortunately, most of the useful functional groups are not compatible with the anionic living polymers of styrene and 1,3-dienes, since their active ends of propagating chains are highly reactive carbanionic species. This means that it is difficult to produce anionic living polymers from styrene and 1,3-dienes containing functional groups.

In order to overcome this difficulty, we have been developing a new strategy for a recent few years.[1,2] The strategy involves the anionic living polymerization of a suitably protected monomer, followed by deprotection of the protecting group from the resulting polymer to regenerate the original functional group. If this synthetic route, e.g., protection–anionic living polymerization–deprotection, could be ideally realized, it would provide a general synthetic route to obtain new living polymers derived from functional monomers that do not normally polymerize under the conditions of anionic polymerization. As a result, the range of anionic polymers should be broadened considerably. Largely through our pioneering works based on the above-mentioned strategy, polystyrenes with a variety of mainly para-substituted functional groups (OH, CH$_2$CH$_2$OH, NH$_2$, CH$_2$NH$_2$, CH$_2$CH$_2$NH$_2$, CHO, COCH$_3$, COOH, C≡CH) and poly[(2-hydroxyethyl) methacrylate] have been successfully synthesized.[3] As expected, the resulting polymers have functional groups in all monomer units as well as predictable molecular weights and nearly monodispersed molecular weight distributions that are the desirable characteristics of their parent living polymers. Such well-defined functional polymers are not accessible through any other methods reported so far.

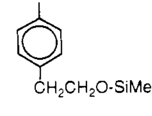
Scheme I



We have previously demonstrated that a *tert*-butyldimethylsilyl group satisfactorily protects the hydroxy groups of 4-vinylphenol[4,5] and 2-(4-vinylphenyl)ethanol[6,7] under the conditions of anionic living polymerization. Actually, the silyl-protected monomers, **1a** and **3a**, were found to undergo anionic living polymerization, followed by deprotection of the silyl groups to afford the well-defined poly(4-vinylphenol) and poly[2-(4-vinylphenyl)ethanol], respectively, as shown in Scheme I.



(1a)



(3a)

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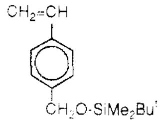
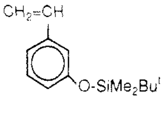
By contrast, we failed under identical conditions to anionically polymerize *tert*-butyldimethylsilyl ether of (4-vinylphenyl)methanol (**2a**), although structurally similar to **1a** and **3a**.[8] This contrary and puzzling result prompted us to investigate the structural influence of related monomers on the anionic polymerization.

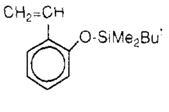


(2a)

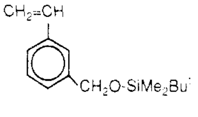
In the present study, we have examined more details of the anionic polymerization of **2a**. In addition, we also focus on the anionic polymerization behaviors of the meta and ortho isomeric monomers (**1b**–**3b**, **1c**–**3c**) in order to ascertain whether these monomers undergo anionic living polymerization or not. For this purpose, the following six additional monomers were synthesized and polymerized. The implications for the methylene number between the hydroxy group and phenyl ring, substituted positions, and the effect of *tert*-butyldimethylsilyl protection of hydroxy groups will be examined.



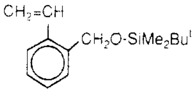
(1b)



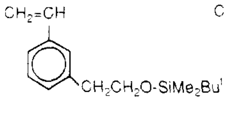
(1c)



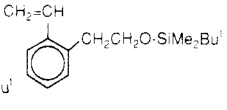
(2b)



(2c)



(3b)



(3c)

Experimental Section

Materials. Tetrahydrofuran (THF) was refluxed over a sodium wire for 6 h and then distilled over $LiAlH_4$ under a nitrogen atmosphere. THF was then distilled from its sodium naphthalenide solution on the vacuum line. Naphthalene was purified by sublimation. Commercially available butyllithium (BuLi) was used without purification. Cumylpotassium was prepared by the reaction of cumyl methyl ether with a Na–K alloy in THF according to the previous method.[9] The concentration was determined by a colorimetric titration of its characteristic red color to colorless endpoint with standardized octanol in a sealed reactor with break-seals. Metal naphthalenides were prepared by the reaction of naphthalene with a small excess of either lithium or potassium in THF. The mixtures were stirred for 12 h at room temperature, and the unreacted metals were removed by filtration to afford characteristic green-colored solutions. The concentrations were determined by the colorimetric titration as described above. These operations (preparation and titration) were performed in sealed reactors with break-seals. Oligo(α-methylstyryl)lithium, -potassium, -dilithium, and -dipotassium were freshly prepared just prior to the polymerization from butyllithium, cumylpotassium, lithium naphthalenide, and potassium naphthalenide and a 3–5 M quantity of α-methylstyrene in THF at 30 °C for 0.5 min and then −78 °C for 10–20 min. Phenylmagnesium chloride was prepared under an atmosphere of nitrogen by the reaction of chlorobenzene with excess Mg in THF. Complete disappearance of chlorobenzene was checked by gas chromatography. Benzylmagnesium chloride was prepared under a nitrogen atmosphere by the reaction of benzyl chloride with excess Mg in THF at 0 °C. Benzyl chloride was found to be completely reacted by gas chromatography.

Monomers. Styrene and α-methylstyrene were washed with 5% NaOH and water and then dried over $MgSO_4$. They were distilled over CaH_2 under a nitrogen atmosphere. Benzylmagnesium chloride (10 mL, 0.25 M in a THF solution) was added to styrene or α-methylstyrene (10–15 g). The mixture was degassed on the vacuum line and stirred at 25 °C for 0.5 h. Styrene or α-methylstyrene was then distilled on the vacuum line into the ampule with break-seals inside of which was prewashed with sodium naphthalenide in THF. These monomers were diluted with THF and divided into several ampules with break-seals. The silyl-protected monomers were prepared according to the methods as described later and were purified by repeated fractional distillations over CaH_2 under a nitrogen atmosphere. Similar to the case of styrene, phenylmagnesium chloride in THF was added to each of the monomers and the monomer was distilled on the vacuum line.

(3-Vinylphenoxy)*tert*-butyldimethylsilane (1b). 3-Vinylphenol[10] (2.78 g, 23.2 mmol) and imidazole (4.04 g, 59.4 mmol) were weighed into a predried 50-mL flask under an atmosphere of nitrogen. Anhydrous DMF (15 mL) was added to dissolve them. A solution of *tert*-butyldimethylsilyl chloride (4.49 g, 29.8 mmol) in dry DMF (15 mL) was added dropwise during 30 min at 0 °C. After addition, the solution was allowed to warm at room temperature and stirred for 10 h. Aqueous 5% NaOH was carefully added. The mixture was extracted with diethyl ether, and the organic layer was washed with 5% NaOH and water and dried over $MgSO_4$. After filtration and removal of the solvent, distillation of the resulting oil under reduced pressure gave pure compound **1b** as a colorless liquid (4.69 g, 86%): bp 56–59 °C (0.1 mmHg); 90-MHz ^1H NMR ($CDCl_3$) δ 7.29–6.53 (5H, m, Ar and CH=), 5.59 (1H, dd, J = 17.6 and 1.1 Hz, CH_2=), 5.11 (1H, dd, J = 10.8 and 1.1 Hz, CH_2=), 1.02 (9H, s, $SiCCH_3$), 0.23 (6H, s, $SiCH_3$); 23-MHz ^{13}C NMR ($CDCl_3$) δ −4.3 ($SiCH_3$), 18.3 (SiC–), 25.9 ($SiCCH_3$), 113.9 (CH_2=), 117.9 (Ar C2), 119.6 (Ar C4 and C6), 129.5 (Ar C5), 136.9 (CH=), 139.2 (Ar C1), 156.0 (Ar C3); IR (KBr) 1253, 988, 962, 907, 839, 789 cm^{-1}. Anal. Calcd: C, 71.73; H, 9.46. Found: C, 71.71; H, 10.01.

(2-Vinylphenoxy)*tert*-butyldimethylsilane (1c). Starting with 2-vinylphenol,[11] fractional distillation at 55–58 °C (1 mmHg) gave **1c** as a colorless liquid in 68% yield by using the same procedure as in the preparation of **1b**: 90-MHz ^1H NMR ($CDCl_3$) δ 7.57–6.51 (5H, m, Ar and CH=), 5.67 (1H, dd, J = 17.6 and 1.1 Hz, CH_2=), 5.21 (1H, dd, J = 10.8 and 1.1 Hz, CH_2=), 1.03 (9H, s, $SiCCH_3$), 0.21 (6H, s, $SiCH_3$); 23-MHz ^{13}C NMR ($CDCl_3$) δ −4.1 ($SiCH_3$), 18.4 (SiC–), 25.9 ($SiCCH_3$), 113.6 (CH_2=), 119.7 (Ar C3), 121.4 (Ar C5), 126.1 (Ar C6), 128.7 (Ar C4), 129.2 (Ar C1), 132.1 (CH=), 153.0 (Ar C2). Anal. Calcd: C, 71.73; H, 9.46. Found: C, 71.51; H, 9.35.

2-, 3-, and 4-Vinylbenzaldehydes. 2-Vinylbenzaldehyde was prepared by the reaction of the Grignard reagent of 2-bromosytrene and DMF previously reported.[12] 2-Bromostyrene (18.3 g, 100 mmol) in THF (50 mL) was added slowly to Mg (3.55 g, 150 mg atom) in THF (150 mL) at 0 °C under a nitrogen atmosphere. Stirring was continued for 1 h at room temperature. Then, dry DMF (10.0 g, 137 mmol) in THF (50 mL) was added dropwise to the Grignard solution at 0 °C over a period of 1 h. The mixture was allowed to stand for 6 h at room temperature. It was poured into ice-cold saturated NH_4Cl, extracted with ether. The combined organic layer was washed with water and dried over $MgSO_4$. After filtration and evaporation, the remaining pale yellow oil was distilled at 67–70 °C (1 mmHg) to give 9.90 g (75 mmol, 75%) of 2-vinylbenzaldehyde as a pale yellow liquid. More than 99.5% purity was obtained by fractionally distilling twice. Similarly, 3- and 4-vinylbenzaldehydes were prepared in 70–85% yields from the reactions of (3-vinylphenyl)magnesium bromide, (4-vinylphenyl)magnesium chloride, and DMF in THF, respectively.

(2-, 3-, and 4-Vinylphenyl)methanols. (2-Vinylphenyl)methanol was prepared by the reduction of 2-vinylbenzaldehyde with $NaBH_4$. To a solution of $NaBH_4$ (1.71 g, 45 mmol) in ethanol (50 mL) and benzene (10 mL) was added dropwise a solution of 2-vinylbenzaldehyde (5.83 g, 44 mmol) in ethanol (10 mL) at 0 °C. The mixture was allowed to warm slowly to room temperature and stirred for 2 h. It was then cooled to 0 °C and acidified by slow addition of 2 N HCl. The organic layer was separated, and the aqueous layer was extracted three times with diethyl ether.

The combined organic extracts were washed with water, dried over $MgSO_4$, and concentrated under reduced pressure to leave crude (2-vinylphenyl)methanol (5.16 g, 39 mmol, 85%) as a pale yellow oil. The purity of the crude product was estimated to be about 95% by NMR. *Caution*! It gradually polymerizes on standing even with added *tert*-butylcatechol at 0 °C. Therefore, (2-vinylphenyl)methanol was immediately used in the next reaction without further purification. Several attempts failed to purify it by distillation under reduced pressure due to the occurrence of undesirable polymerization. Similarly, (3-vinylphenyl)- and (4-vinylphenyl)methanols were prepared in 80–90% yields by the reductions of 3- and 4-vinylbenzaldehydes with $NaBH_4$. Both (vinylphenyl)methanols were estimated by their NMR spectra to be 93–97% pure and used without purification in the next silylation reactions. In these cases, undesirable polymerizations also occurred during the distillations, similar to the case of ortho isomer described above. No purified products were obtained at all by the distillations under reduced pressure.

[(4-Vinylphenyl)methoxy]*tert*-butyldimethylsilane (2a). **2a** was obtained by the reaction of (4-vinylphenyl)methanol with *tert*-butyldimethylsilyl chloride similar to the method described above. Fractional distillation at 81–82 °C (1 mmHg) gave a colorless liquid (85%): 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.42–7.20 (4H, m, Ar), 6.70 (1H, dd, J = 17.5 and 11.0 Hz, CH=), 5.70, 5.19 (2H, dd, J = 17.5 and 11.0 Hz, CH_2=), 4.71 (2H, s, $-OCH_2-$), 0.92 (9H, s, $SiCCH_3$), 0.08 (6H, s, $SiCH_3$); 23-MHz ^{13}C NMR ($CDCl_3$) δ -5.1 ($SiCH_3$), 18.5 (SiC–), 26.1 ($SiCCH_3$), 64.9 (CH_2OSi), 113.3 (CH_2=), 126.2 (Ar C2), 126.3 (Ar C3), 136.5 (Ar C1), 136.8 (CH=), 141.2 (Ar C4); IR 1257, 1118, 1094, 990, 905 cm^{-1}.

[(3-Vinylphenyl)methoxy]*tert*-butyldimethylsilane (2b). **2b** was obtained by the reaction of (3-vinylphenyl)methanol with *tert*-butyldimethylsilyl chloride similar to the method described above. Fractional distillation at 80–83 °C (1 mmHg) gave a colorless liquid of **2b** (70%): 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.36 (1H, s, Ar C2-H), 7.25 (1H, d, J = 4.2 Hz, Ar C6-H), 7.24 (1H, s, Ar C5-H), 7.18 (1H, d, J = 4.2 Hz, Ar C4-H), 6.82 (1H, dd, J = 17.6 and 10.8 Hz, CH=), 5.73, 5.22 (2H, dd, J = 17.6 and 10.8 Hz, CH_2=), 4.74 (2H, s, $-OCH_2-$), 0.95 (9H, s, $SiCCH_3$), 0.10 (6H, s, $SiCH_3$); 23-MHz ^{13}C NMR ($CDCl_3$) δ -5.1 ($SiCH_3$), 18.5 (SiC), 26.1 ($SiCCH_3$), 65.0 (CH_2OSi), 113.8 (CH_2=), 124.0 (Ar C2), 125.0 (Ar C6), 125.7 (Ar C4), 128.5 (Ar C5), 137.1 (CH=), 137.7 (Ar C1), 141.8 (Ar C3); IR (KBr) 1256, 1105, 1084, 990, 905 cm^{-1}. Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74. Found: C, 71.73; H, 9.62.

[(2-Vinylphenyl)methoxy])*tert*-butyldimethylsilane (2c). **2c** was obtained by the reaction of (2-vinylphenyl)methanol with *tert*-butyldimethylsilyl chloride similar to the method described above. Fractional distillation at 68–69 °C (1.5 mmHg) gave a colorless liquid (77%): 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.54–7.20 (4H, m, Ar), 6.93 (1H, dd, J = 17.4 and 11.0 Hz, –CH=), 5.63, 5.29 (2H, dd, J = 17.4 and 11.0 Hz, CH_2=), 4.77 (2H, s, $-OCH_2-$), 0.92 (9H, s, $SiCCH_3$), 0.08 (6H, s, $SiCH_3$); 23-MHz ^{13}C NMR ($CDCl_3$) δ -5.2 ($SiCH_3$), 18.5 (SiC–), 26.1 ($SiCCH_3$), 63.3 (CH_2OSi), 115.9 (CH_2=), 125.6 (Ar C6), 127.1 (Ar C3), 127.3 (Ar C5), 127.8 (Ar C4), 134.1 (CH=), 135.9 (Ar C1), 138.2 (Ar C2); IR (KBr) 1255, 1120, 1077, 987, 912 cm^{-1}.

2-(2-Vinylphenyl)ethanol and 2-(3-Vinylphenyl)ethanol. To a solution of the Grignard reagent from 2-bromostyrene (7.58 g, 41.4 mmol) and Mg (1.62 g, 66.7 mg atom) in THF (40 mL) was added carefully dropwise during 30 min a solution of ethylene oxide (2.19 g, 49.8 mmol) in THF (10 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for an additional 1 h. After standard workup (addition of a NH_4Cl saturated solution and extraction with diethyl ether), fractional distillation of the crude product at 70–71 °C (1 mmHg) gave 2-(2-vinylphenyl)ethanol as a colorless liquid (4.00 g, 27 mmol, 65%). Similarly, 2-(3-vinylphenyl)ethanol was obtained in 56% yield from the reaction of (3-vinylphenyl)magnesium bromide with ethylene oxide in THF. Fractional distillation at 75–77 °C (1 mmHg) gave the desired product as a colorless liquid. Both products were identified by ^{1}H and ^{13}C NMR spectra.

[2-(3-Vinylphenyl)ethoxy]*tert*-butyldimethylsilane (3b). **3b** was obtained by the reaction of 2-(3-vinylphenyl)ethanol with *tert*-butyldimethylsilyl chloride similar to the method above. Fractional distillation at 90–91 °C (1 mmHg) gave a colorless liquid (90%): 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.20–7.11 (4H, m, Ar), 6.67 (1H, dd, J = 17.6 and 10.8 Hz, CH=), 5.69 (1H, dd, J = 17.6 and 1.1 Hz, CH_2=), 5.18 (1H, dd, J = 10.8 and 1.1 Hz, CH_2=), 3.78 (2H, t, J = 7.0 Hz, CCH_2O-), 2.78 (2H, t, J = 7.0 Hz, CH_2CO), 0.84 (9H, s, $SiCCH_3$), -0.05 (6H, s, $SiCH_3$); 23-MHz ^{13}C NMR ($CDCl_3$) δ -5.3 ($SiCH_3$), 18.4 (SiC), 26.1 ($SiCCH_3$), 39.7 (*C*CO), 64.5 (C*C*O), 113.7 (CH_2=), 124.2 (Ar C6), 127.2 (Ar C2), 128.4 (Ar C4), 128.7 (Ar C5), 137.1 (CH=), 137.6 (Ar C1), 139.6 (Ar C3); IR (KBr) 1255, 1100, 990, 906, 836, 775 cm^{-1}.

[2-(2-Vinylphenyl)ethoxy]*tert*-butyldimethylsilane (3c). **3c** was obtained by the reaction of 2-(2-vinylphenyl)ethanol with *tert*-butyldimethylsilyl chloride similar to the method above. Fractional distillation at 72–74 °C (1 mmHg) gave a colorless liquid (60%): 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.70–7.20 (4H, m, Ar), 7.11 (1H, dd, J = 17.4 and 10.8 Hz, CH=), 5.70 (1H, dd, J = 17.4 and 1.1 Hz, CH_2=), 5.37 (1H, dd, J = 10.8 and 1.1 Hz, CH_2=), 3.84 (2H, t, J = 7.3 Hz, CCH_2O-), 2.99 (2H, t, J = 7.3 Hz, CH_2CO), 0.94 (9H, s, $SiCCH_3$), 0.05 (6H, s, $SiCH_3$); 23-MHz ^{13}C NMR ($CDCl_3$) δ -5.3 ($SiCH_3$), 18.4 (SiC), 26.1 ($SiCCH_3$), 36.9 (*C*CO), 64.0 (C*C*O), 115.6 (CH_2=), 125.9 (Ar C6), 126.7 (Ar C5), 127.7 (Ar C4), 130.6 (Ar C3), 134.9 (CH=), 136.4 (Ar C2), 137.2 (Ar C1); IR (KBr) 1256, 1111, 1093, 990, 835, 774 cm^{-1}.

Polymerization Procedures. All the polymerizations were carried out at -78 °C for 10–60 min with shaking under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with break-seals. The desired charge of monomer in a THF solution was added to a solution of initiator with well-shaking. Both solutions must be kept at -78 °C. The polymerization was then terminated with degassed methanol. The polymer was precipitated by pouring the reaction mixture into a large amount of methanol. It was purified by repeated precipitation (three times) from THF solution to methanol and freeze-dried. Similarly, block copolymerization was carried out by a sequential polymerization of **2b** with styrene.

Deprotection of Silyl Groups from Polymers. Deprotection of the *tert*-butyldimethylsilyl group from poly(**2b**) with either F^- or H^+ was demonstrated as a typical experimental example. Poly(**2b**) (0.22 g, 0.88 mmol calculated as a monomer unit) was added to $(C_4H_9)_4NF$ (5.0 mL of a 1.0 M THF solution). The reaction mixture was stirred at room temperature for 1 h. The polymer was then precipitated by pouring the mixture into a NH_4Cl saturated aqueous solution. It was washed with water, purified by reprecipitation from an ethanol solution to hexane twice, and dried by vacuum pump. The yield of polymer (0.12 g, 0.88 mmol) was quantitative.

Similarly, an acid-promoted deprotection reaction of poly(**2b**) (0.48 g, 1.9 mmol calculated as a monomer unit) was carried out in 0.6 N HCl/aqueous THF (10 mL) (THF/H_2O, 20/1, v/v) at room temperature for 0.5 h. The polymer was isolated by precipitation into water. It was washed with water, purified by reprecipitation from ethanol to hexane twice, and dried by vacuum pump. A quantitative yield of polymer was also obtained in this case (0.26 g, 1.9 mmol).

Both the polymers thus obtained were identified as poly[(3-vinylphenyl)methanol] by their IR and ^{1}H NMR spectra: 90-MHz ^{1}H NMR (CD_3OD) δ 7.3–6.2 (4H, m, Ar), 4.5 (2H, s, CH_2O-), 2.3–1.1 (3H, m, CH_2CH); 90-MHz ^{1}H NMR (DMSO-d_6) δ 7.3–6.0 (4H, m, Ar), 5.0 (1H, s, OH), 4.4 (2H, s, CH_2O-), 2.3–1.1 (3H, m, CH_2CH); IR (KBr) 3400, 1021 cm^{-1}.

Similarly, quantitative deprotection of the *tert*-butyldimethylsilyl groups from the polymers of **1a,b** and **3a–c** was performed by treatment with either F^- or H^+. In these cases, the conditions varied slightly to complete the deprotection reactions by the structure and molecular weight of the polymers used.

Benzoylation Reaction of Poly(2b). To a solution of benzoic anhydride (1.85 g, 8.2 mmol) in dry pyridine (1.5 mL) was added slowly poly[(3-vinylphenyl)methanol] (0.10 g, 0.75 mmol calculated as a monomer unit) dissolved in dry pyridine (1.5 mL) at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at 25 °C for 48 h. The polymer was isolated by precipitation into methanol, purified by reprecipitation from THF to methanol, and freeze-dried. Yield of polymer was quantitative (0.18 g, 0.75 mmol): 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.9 (2H, m, C2-H of C_6H_5CO-), 7.3 (3H, m, C3-H and C4-H of C_6H_5CO-), 7.2–6.0 (4H, m, Ar), 5.0 (2H, s, CH_2O), 2.3–0.7 (3H, m, CH_2CH).

Similarly, benzoylation of the other deprotected polymers was carried out and the degrees of benzoylation were found to be quantitative in all samples by ^{1}H NMR analyses.

Measurement. Infrared (IR) spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6-MHz ^{1}H, 22.53-MHz ^{13}C) mainly in $CDCl_3$. Chemical shifts were reported in ppm downfield relative to $(CH_3)_4Si$ (δ 0) for ^{1}H NMR spectra and $CDCl_3$ (δ 77.1) for ^{13}C NMR spectra as standard. 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 G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) were used. Vapor pressure osmometry (VPO) measurements for absolute $\bar{M}_n$ determination were made with a Corona 117 instrument in a benzene solution with a highly sensitive thermoelectric couple and equipment of very exact temperature control. Therefore, $\bar{M}_n$s up to 10^5 could be determined within an analytical error of ±5%.

Results and Discussion

Several papers state that *tert*-butyldimethylsilyl ethers are compatible with reaction conditions involving highly reactive nucleophiles and basic reagents such as Grignard reagents and organolithium compounds.[13,14] Some organolithium compounds containing *tert*-butyldimethylsilyl ether linkages have also been synthesized.[14-20] These facts are especially valuable when one needs to protect the hydroxy groups of monomers under the conditions of anionic living polymerization where reactive carbanionic species are always present.

We previously demonstrated the successful protection of the hydroxy groups of styrene derivatives, **1a** and **3a**, with a *tert*-butyldimethylsilyl group during the course of the anionic polymerizations.[4-7] Stable living polymers derived from **1a** and **3a** could be obtained. Therefore, we first anticipated that the *tert*-butyldimethylsilyl ether of (4-vinylphenyl)methanol, **2a**, would undergo anionic living polymerization without difficulty. Unexpectedly, no polymer could be produced under a typical anionic polymerization condition where either sodium naphthalenide or oligo (α-methylstyryl)disodium was used as an initiator in THF at −78 °C. Although the inability of **2a** to polymerize may possibly be attributed to the monomer structure, e.g., benzyl silyl ether, the result seems to be strange, taking into account the successful living polymerization of **1a** and **3a**. This contrasting result prompts us to study in more detail the anionic polymerizations of the related silyl-protected monomers. For this purpose as described in the introduction, we synthesized a total of nine styrene derivatives with *tert*-butyldimethylsilyl-protected hydroxy groups, **1a**–**c**, **2a**–**c**, and **3a**–**c**, and examined their anionic polymerization behaviors.

Anionic Polymerization of 1a–c. In 1982, we reported the first successful demonstration of the anionic living polymerization of **1a** and synthesis of linear poly(4-vinylphenol)s with uniform and controllable chain lengths by complete removal of the silyl protecting group from the polymer.[4] In addition, novel well-defined block copolymers of **1a** with styrene and isoprene could be obtained by using the living polymer of **1a**.

Then, we have carried out the anionic polymerization of the meta-substituted monomer, **1b**, in attempting to obtain a living polymer. The initiators used were *n*-butyllithium and lithium and potassium naphthalenides capped with small excesses of α-methylstyrene. Intensive color changes to orange or dark red were observed during the polymerizations. These clearly indicate the existence of polystyryl anions derived from **1b**. The colors were stable at −78 °C even for 24 h but disappeared immediately by quenching with methanol. Yields of polymers were quantitative in all runs. The results are summarized in Table I.

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

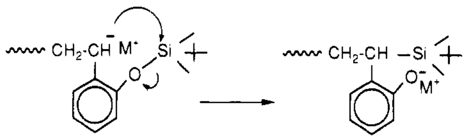
monomer	initiator		α-MeSt,[b]	$10^{-3}\bar{M}_n$		
1b, mmol	type	mmol	mmol	calcd	obsd[c]	$\bar{M}_w/\bar{M}_n$[d]
3.27	Li-Nap[e]	0.221	0.443	7.4	8.0 (6.1)[h]	1.04
2.08	K-Nap[f]	0.969	0.348	11	12 (8.8)	1.08
2.10	K-Nap	0.0643	0.211	17	18 (13)	1.05
2.56	Li-Nap	0.0490	0.360	26	24 (20)	1.06
2.73	BuLi[g]	0.0242	0.316	28	54 (40)	1.04

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

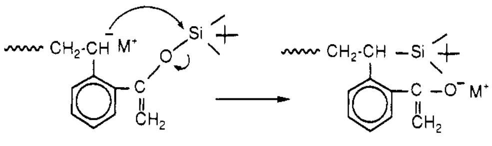
As can be seen, there is quite a good agreement between the values of $\bar{M}_n$ calculated and observed except for one experiment using *n*-butyllithium which afforded a polymer with higher molecular weight than the predicted value. It is likely to be explained by insufficient dissociation of *n*-butyllithium to reduce active species. The polymers all are observed to have narrow molecular weight distributions, their $\bar{M}_w/\bar{M}_n$ values being around 1.05. Accordingly, the results strongly indicate living character of the polymerization of **1b** similar to the case of **1a**. The success of the anionic living polymerization of **1b** again demonstrates that a *tert*-butyldimethylsilyl group is able to effectively protect the phenolic hydroxy group during the polymerization. In other words, the ^{t}BuMe$_2$Si–O bond is stable enough toward the propagating chain ends from **1a** and **1b** that they are highly reactive carbanionic species.

By contrast, when the ortho-substituted isomer, **1c**, was polymerized under exactly the same conditions, no appreciable polymerization occurred with any of the following initiators: *n*-butyllithium, sodium and potassium naphthalenides, and oligo(α-methylstyryl)dipotassium. Most of **1c** was recovered unchanged from all reaction mixtures without desired polymeric materials being detected. Thus, the anionic polymerization of **1c** was not successful.

As previously described, *tert*-butyldimethylsilyl ethers are stable toward the highly reactive carbanionic species like anionic initiators used above. Their stabilities are also obvious from the results that the anionic living polymerizations of **1a** and **1b** proceed without difficulty. However, it has been reported that some organolithium compounds can intramolecularly react with silyl groups.[21-23] For example, anionic silyl rearrangements in *tert*-butyldimethylsilyl enol ethers and even the sterically demanding triisopropylsilyl alkyl ethers readily occur via intramolecular nucleophilic attack at silicon atoms by their carbanions. This means that the carbanion potentially reacts with the silyl group when they are present at a suitable spatial position to each other. Therefore, we suspect a similar intramolecular reaction between the carbanion and the silyl group as a possible side reaction candidate to interfere with the polymerization of **1c**. The reaction might be further promoted by the fact that a phenolate anion is generally a better leaving group than those of enolate and alkolate. The following is a plausible mechanism which postulates involvement of the five-membered intermediate, e.g., 1,4 O → C silyl rearrangement as shown below:



Thus, the ortho-substituted monomer **1c** would not polymerize under the conditions of typical anionic polymerization, whereas both the para and meta isomers underwent living polymerization without difficulty. Very recently, in the polymerization of the *tert*-butyldimethylsilyl enol ether of 2-vinylacetophenone, we have also encountered the difficulty to anionically polymerize this monomer, probably due to a similar termination reaction occurring during the polymerization as follows:[3e]



Anionic Polymerization of 2a–c. The different behavior of polymerization by the substitution pattern has also been observed in the anionic polymerizations of *tert*-butyldimethylsilyl ethers of (vinylphenyl)methanols, **2a–c**. The same picture found in the preceding section, however, was not shown in the polymerizations. As mentioned before, initial attempts to polymerize the para-substituted **2a** were not successful with sodium naphthalenide and oligo(α-methylstyryl)disodium in THF at −78 °C. No polymer was obtained, and the monomer unchanged was recovered nearly quantitatively in each case.[8]

We set up here again to polymerize **2a** with various anionic initiators to explore the polymerization ability. The polymerizations were carried out with use of the following initiators: butyllithium, lithium and potassium naphthalenides, and oligo(α-methylstyryl)dilithium and -dipotassium. Characteristic green or dark red colors of the anionic initiators employed immediately disappeared on addition of **2a**. It was again found that polymeric material was not produced and most of the starting monomer was recovered even after 24 h from each of all the cases. Thus, the polymerization of **2a** failed under typical anionic conditions.

On the other hand, the meta-substituted isomer, **2b**, has been found to polymerize completely under exactly the same conditions. For example, the desired charge of **2b** was added to oligo(α-methylstyryl)dipotassium in THF at −78 °C, with resulting formation of a deep red color, indicating the existence of a polystyryl anion from **2b**. The color remains stable as long as the temperature is kept at −78 °C but immediately disappears on adding a few drops of methanol. The polymer was obtained quantitatively by precipitation in methanol.

The resulting polymer yielded a ^{1}H NMR spectrum that showed two singlets from the methyl protons of *tert*-butyl and dimethylsilyl groups at 0.95 and 0.10 ppm, in reasonable integral ratios with those of other signals. The IR spectrum contained strong absorptions at 1255 and 1079–1105 cm^{-1} for the Si–CH$_3$ and Si–O–C bonds, respectively. These indicate no cleavage of the *tert*-butyldimethylsilyl protecting group during the above workup. Accordingly, characterization of the polymer by SEC and VPO measurements could be performed in the form of poly(**2b**) just like the cases of polymers from **1a** and **1b**.

The values of $\bar{M}_n$ calculated and observed and $\bar{M}_w/\bar{M}_n$ for the series of poly(**2b**) obtained not only with oligo(α-methylstyryl)dipotassium but with the other initiators are listed in Table II. As can be seen, the agreement between the observed $\bar{M}_n$ values by VPO and the predicted ones calculated from [M] to [I] ratios is satisfactory within analytical errors. Inspection of the SEC charts shows that the polymers all possess single peaks with narrow distributions of the molecular weight, the values of $\bar{M}_w/\bar{M}_n$ being around 1.1. These results as well as the characteristic red colorations in the polymerization systems clearly indicate that **2b** gives a normal anionic living polymer.

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

monomer	initiator		α-MeSt,[b]	$10^{-3}\bar{M}_n$		
2b, mmol	type	mmol	mmol	calcd	obsd[c]	$\bar{M}_w/\bar{M}_n$[d]
3.03	K-Nap[e]	0.145	0.324	11	10 (8.8)[i]	1.08
1.18	Li-Nap[f]	0.0519	0.256	12	13 (11)	1.15
13.7	cumyl K[g]	0.0989	0.164	35	33 (25)	1.13
4.07	BuLi[h]	0.0244	0.449	44	45 (38)	1.19

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

Table III. Block Copolymerization of 2b with Styrene at −78 °C in THF with Oligo(α-methylstyryl)dipotassium[a]

type of block copolymer	A monomer	B monomer	block copolymer[b] (homopolymer)[c]	
			$10^{-3}\bar{M}_n$(calcd)	$10^{-3}\bar{M}_n$(obsd)[d]
B-A-B	**2b**	styrene	34 (12)	38 (12)

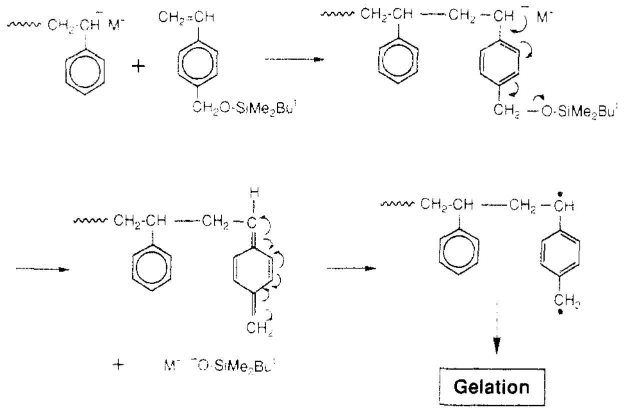
[a] Yields of polymers were quantitative. [b] Polymerization times at the first and at the second stages were both 0.5 h. [c] Homopolymer was obtained at the first stage of polymerization. [d] $\bar{M}_n$(obsd) was obtained by VPO in a benzene solution.

The feasibility of synthesizing a new type of well-defined block copolymer containing poly(**2b**) segment was demonstrated by the sequential anionic living polymerization of **2b** and styrene. A quantitative formation of poly(styrene-*b*-**2b**-*b*-styrene) with desired structures could be elucidated by the analytical results of the resulting polymer by ^{1}H NMR, SEC, and VPO. Clearly, as can be seen in Table III, the block copolymer possesses a predictable molecular weight and composition as well as a narrow molecular weight distribution. The result also provides very strong evidence for the living character of the anionic polymerization of **2b**.

Difficulty was again encountered in the polymerization of the ortho isomeric monomer, **2c**. Only trace amounts of polymeric material could be otained. For example, when **2c** was polymerized with either oligo(α-methylstyryl)dilithium or the corresponding potassium salt in THF at −78 °C, the characteristic colors of both initiators disappeared immediately on addition of monomer. The polymeric materials were obtained in 6 and 10%, respectively, after 30 min. Their SEC charts exhibited very broad molecular weight distributions in $\bar{M}_n$ ranges from 10^3 to 10^6. Furthermore, these polymers were found by IR measurement to be mainly composed of an α-methylstyrene unit that came from initiator residues. Therefore, participation of **2c** in the polymerization is almost negligible.

Among the *tert*-butyldimethylsilyl ethers of (vinylphenyl)methanols, both the para and ortho isomers, **2a** and **2c**, would not undergo appreciable polymerization. As shown earlier anionic living polymerization of the meta-substituted **2b** is clearly realized under exactly the same

Scheme II



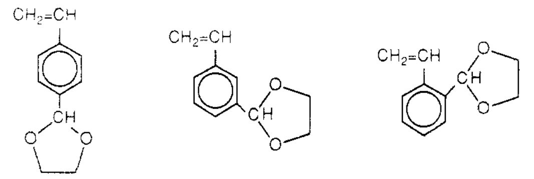
conditions. We first consider that the proton abstraction of a benzylic methylene group and/or the silicon attack by the carbanions of initiators and propagating chain ends are the possible candidates for termination reactions occurring in the polymerizations of **2a** and **2c**.[24] The possibility of such reactions can be, however, ruled out from the observation that a living polystyrene anion with a potassium cation is stable enough in the presence of a large excess of *tert*-butyldimethylsilyl benzyl ether as a monomer model compound. The success of the anionic living polymerization of **2b** may also exclude the possibility of such reactions. Accordingly, the occurrence of undesirable termination reactions may be inherent to the substituents at ortho and para positions.

Furthermore, anomalous behaviors of **2a** and **2c** were observed in the reactions with a living polystyrene initiated with potassium naphthalenide. Addition of either **2a** or **2c** to the living polystyrene always resulted in the formation of insoluble gelatinous materials, along with very small amounts of soluble polymers with broad molecular weight distributions in THF at −78 °C. The IR spectra showed that the materials consisted mainly of polystyrenes. They are probably cross-linked, based on the insolubility in organic solvents. Most of the starting monomers were recovered in both cases, indicating that only a few monomers might participate in the reaction leading to the cross-linking of living polystyrene.

On the basis of the above results, we propose an alternative and most likely reaction pathway by which the polymerization results of **2a** and **2c** can be explained. The proposed pathway is that the carbanion at the polymer chain end may induce 1,6-elimination for the para isomer or 1,4-elimination for the ortho isomer. The intermediate of such an elimination must be very reactive *p*-xylylene (or *o*-xylylene), which might react readily with each other to result in a cross-linked polymer network as shown in Scheme II where the case of **2c** is illustrated.

Some suggestive observations and a reaction mechanism related to the above pathway have been previously reported by Rickborn and co-workers in the reactions of methyl *o*-methylbenzyl ether and the derivatives with strong bases which are nonnucleophilic.[25-27] They proposed base-induced 1,4-elimination, generating a reactive *o*-xylylene intermediate. The key point of their mechanism is that it is effective for ortho-substituted and probably para-substituted benzyl ethers. On the other hand, the meta-substituted isomer is not applicable to the mechanism. These results and mechanism also explain our results of the anionic polymerizations of the three benzyl-type monomers, **2a–c**. In addition, the cross-linking that occurred in the reactions of living polystyrene with **2a** and **2c** can also be satisfactorily explained by the further reactions of very reactive *o*- and *p*-xylylene intermediates.

Very recently, we have observed a similar result in the anionic polymerizations of a series of the 1,3-dioxolanyl-substituted styrene derivatives as shown below:[28]



The polymerization of the meta-substituted styrene was a typical anionic living system, whereas the polymerizations of both the ortho and para isomers were not successful at all. For these results, the same reaction pathways as proposed here are being considered at the present time. Although direct evidence for the proposed mechanism is not obtained yet, it should be noted that the anionic polymerizations of styrenes containing the $(RO)_2CH$ and $Bu^tMe_2SiOCH_2$ groups, e.g., alkyl benzyl ether and silyl benzyl ether types, were significantly influenced by differences of the position of these substituents. Attention should be again called to those who use such monomers in the anionic polymerization.

Anionic Polymerizations of 3a–c. In order to obtain more information on the influence of the substitution pattern at the *p*-, *m*-, or *o*-position and *tert*-butyldimethylsilyl protection upon the anionic polymerization, we have examined the polymerization behaviors of the para-, meta-, and ortho-substituted *tert*-butyldimethylsilyl ethers of 2-(vinylphenyl)ethanols, **3a–c**, where the siloxy groups are separated by two methylene units from the benzene ring.

We previously reported that the para-substituted monomer, **3a**, underwent anionic living polymerization without difficulty.[6,7] The polymers with controllable molecular weights and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ < 1.1) as well as well-defined block copolymers with styrene were obtained under similar polymerization conditions employed here.

The meta and ortho isomers, **3b** and **3c**, were newly synthesized and polymerized with various anionic initiators in THF at −78 °C. The polymerization mixtures always exhibited orange to dark red colors, indicating the formation of polystyryl anions from **3b** and **3c**, respectively. Polymers were obtained quantitatively by precipitation in methanol in both cases. Structures of the polymers obtained were characterized by IR, ^1H and ^{13}C NMR, and elemental analysis. These results clearly showed these polymers to be normal structures produced by vinyl polymerization just like the case of poly(**3a**) previously reported. No cleavage of Si–O bonds in the polymers was observed after purification by 3 times reprecipitation. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values could be directly measured by VPO and SEC in their protected forms. The results are summarized in Table IV.

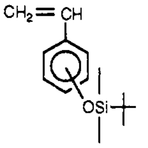
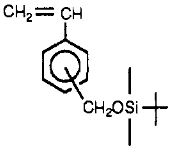
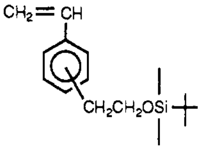
As you can see, there is a fair agreement between the $\bar{M}_n$ values calculated and observed. The SEC curves of all samples are found to have sharp and symmetrically unimodal peaks. The $\bar{M}_w/\bar{M}_n$ values are less than 1.1. These results as well as the observation of red coloration in the systems strongly indicate that both the polymerizations of **3b** and **3c** proceed in a living manner, similar to the polymerization with para-substituted monomer, **3a**. Thus, the anionic living polymerizations of all three isomeric monomers can be successfully achieved for the first time by introducing two methylene units between the siloxy group and the benzene ring.

Table IV. Anionic Polymerizations of 3b and 3c in THF at −78 °C for 1 h[a]

monomer		initiator		α-MeSt,[b]	$10^{-3}\bar{M}_n$		
	mmol	type	mmol	mmol	calcd	obsd[c]	$\bar{M}_w/\bar{M}_n$[d]
3b	2.04	K-Nap[e]	0.0967		11	10 (9.1)[i]	1.06
3b	3.32	BuLi[f]	0.0668	0.195	14	16 (15)	1.07
3b	4.50	s-BuLi[g]	0.0333	0.100	36	38 (35)	1.05
3c	2.49	cumyl K[h]	0.0753		8.7	9.3 (6.3)	1.09
3c	2.36	s-BuLi	0.0569	0.189	11	13 (8.9)	1.04
3c	2.38	K-Nap	0.0718	0.213	18	17 (12)	1.08
3c	2.95	BuLi	0.0516	0.498	17	21 (16)	1.12

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

Table V. Results of Anionic Polymerizations of TBDMS Ethers of Vinylphenols, (Vinylphenyl)methanols, and 2-(Vinylphenyl)ethanols[a]

monomer	para	meta	ortho
	○	○	×
	×	○	×
	○	○	○

[a] ○ indicates living polymerization; × indicates no polymerization.

In summary, in the anionic polymerizations of *tert*-butyldimethylsilyl ethers of vinylphenols, living polymerizations of the para- and meta-substituted monomers were achieved, whereas the polymerization of the ortho isomer failed, probably due to the intramolecular silicon attack by the styryl anion. In a series of *tert*-butyldimethylsilyl-protected (vinylphenyl)methanols, only the meta-substituted monomer was found to undergo anionic living polymerization. No significant polymerization proceeded with either the para or ortho isomer. We proposed that the 1,6- and 1,4-elimination to form reactive xylylene intermediates might occur to prevent these polymerizations. With *tert*-butyldimethylsilyl ethers of 2-(vinylphenyl)ethanol whose siloxy groups were separated from benzene rings by two methylene units, there was no difficulty in the anionic living polymerizations of all three positional isomeric monomers. The results are summarized in Table V.

From these results with use of the structurally similar nine monomers, *tert*-butyldimethylsilyl protection is considered to be essentially effective for both the phenolic and alcoholic hydroxy groups of styrene derivatives under conditions of anionic living polymerization. Nevertheless, difficulties of the anionic polymerizations using **1c**, **2a**, and **2c** are encountered under the same conditions. Therefore, care must be taken in dealing with these silyl-protected monomers. As mentioned before, we have recently observed similar difficulties based on the differences of the substitution pattern of the monomers in the anionic polymerizations of acetal-protected vinylbenzaldehydes[3e] and silyl-protected vinylacetophenones.[28] Therefore, even if a protected functional monomer could undergo anionic living polymerization, the polymerization behaviors of the positional isomeric monomers should be examined.

Deprotection of *tert*-Butyldimethylsilyl Group from Polymers. Complete removal of the protecting group is essential in the synthesis of functional polymers with well-defined chain structures, since separation of the protected and the deprotected forms in the same polymer chain is in principle impossible.

The *tert*-butyldimethylsilyl ethers are known to be stable under neutral to slightly basic conditions in even aqueous solutions. In fact, cleavage of the Si–O bonds in our polymer samples could not be observed within analytical errors by IR and ^{1}H and ^{13}C NMR under the same conditions as above. Therefore, handling of these polymers requires no special care in the steps of isolation and purification. The polymers are directly characterized in their protected forms by VPO and SEC. This is especially convenient in order to ascertain living character of the polymerization.

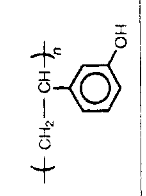
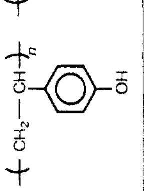
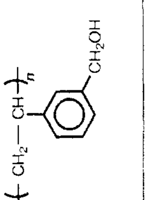
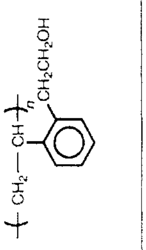
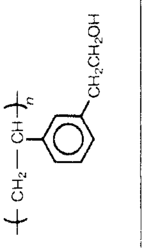
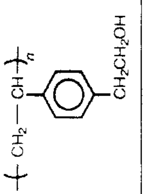
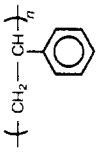
On the other hand, ready and complete deprotection of the *tert*-butyldimethylsilyl group was achieved by treatment with either $(C_4H_9)_4NF$ or a diluted HCl solution, similar to the cases of the corresponding low molecular weight silyl ethers. The *tert*-butyldimethylsilyl ethers of all polymers obtained were found to be cleaved completely within a few hours under the condition with $(C_4H_9)_4NF$ in THF at 25 °C. This was confirmed by IR and ^{1}H NMR. Similarly, quantitative deprotection was also possible by treatment with 0.5–5 N HCl in aqueous THF solutions for 1–24 h. In these cases, the conditions varied slightly to complete the reactions by structure and molecular weight of the polymers used.

The ^{1}H NMR analyses of the resulting polymers always reveal the desired structures of polystyrenes with hydroxy groups. However, analyses of the polymers by SEC are generally questionable especially when the polymers with high molecular weights are measured. The SEC curves were eluted as unsymmetrical peaks with more or less tailings, indicating a strong interaction between the polymer and the SEC column. To overcome this problem, the polymers were benzoylated with benzoic anhydride in dry pyridine and analyzed again by SEC. The chromatograms of the resulting polymers all exhibited symmetrical peaks eluted at reasonable molecular weight regions. The shapes of these benzoylated polymers were found to be nearly identical with those of parent protected polymers in all cases. As a typical example, the chromatograms of poly(**2b**), the poly[(3-vinylphenyl)methanol] after deprotection, and the benzoylated polymer are illustrated in Figure 1. These results indicate no reactions leading to main-chain degradation, branching, or cross-linking during the F$^-$- and H$^+$-promoted deprotection reactions. Accordingly, the resulting polymers from **1a**–**b**, **2b**, and **3a**–**c** must be linear polymers with controllable molecular weights and narrow molecular weight distributions. They have of course phenolic or alcoholic hydroxy groups in all monomer units.

The deprotection reaction for the block copolymers with styrene also proceeded efficiently and cleanly under the same conditions using the corresponding homopolymers. Novel well-defined block copolymers with hydrophilic and hydrophobic segments could thus be obtained.

The polymers with *tert*-butyldimethylsilyl groups are generally soluble in a wide variety of solvents such as

Table VI. Solubilities of Polystyrenes with Hydroxy Groups and Polystyrene[a]

solvent							
hexane	I	I	I	I	I	I	I
benzene	I	I	I	I	I	I	S
toluene	I	I	I	I	I	I	S
carbon tetrachloride	I	I	I	I	I	I	S
chloroform	I	I	I	I	I	I	S
acetone	S	S	I	I	I	I	S
1,4-dioxane	S	S	S	I	S	S	S
THF	S	S	S	I	S	I	S
pyridine	S	S	S	S	S	S	S
DMF	S	S	S	S	S	S	S
ethanol	S	S	S	I	S	S	I
methanol	S	S	S	I	S	S	I
water	I	I	I	I	I	I	I

[a] I, insoluble; S, soluble.

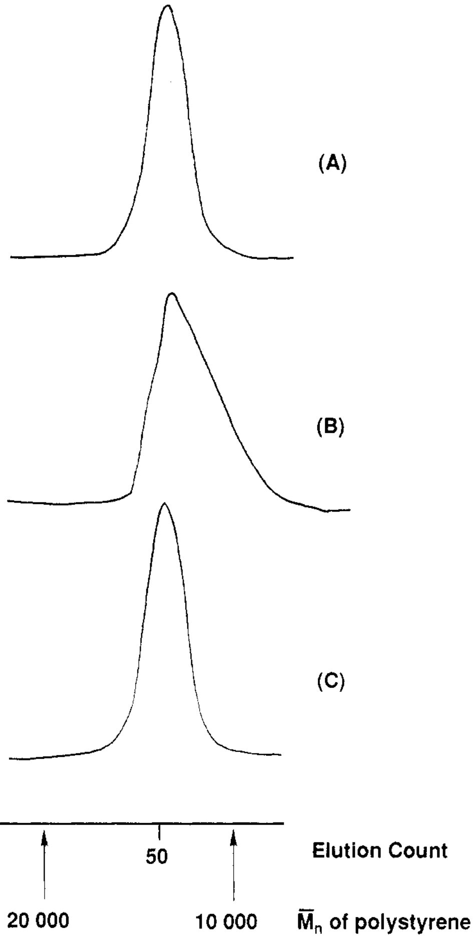


Figure 1. SEC curves of (A) poly(**2b**), (B) poly[(3-vinylphenyl)methanol], and (C) benzoylated polymer.

pentane, hexane, benzene, toluene, carbon tetrachloride, chloroform, dichloromethane, ethyl acetate, acetone, diethyl ether, 1,4-dioxane, THF, and pyridine but insoluble in methanol, ethanol, *N,N*-dimethylformamide (DMF), and water. In contrast, the solubilities of polymers with hydroxy groups differ considerably from the parent silyl-protected polymers and even from each other. The results are summarized in Table VI. The solubility of polystyrene was also listed as a reference. As can be seen, all six polymers obtained here are soluble in pyridine and DMF but insoluble in hexane, benzene, toluene, carbon tetrachloride, chloroform, and water. More interestingly, in some solvents the substitution position and methylene number as well as the difference between phenolic and alcoholic hydroxy groups can affect the solubility considerably. As expected, the solubilities of block copolymers with styrene were between those of both segments and appeared to be dependent upon their chain lengths.

Conclusions

The results described here demonstrate that it is possible to synthesize well-defined polystyrenes with hydroxy side groups by applying anionic living polymerization through the use of *tert*-butyldimethylsilyl protection for hydroxy groups, followed by complete deprotection. The polymers obtained by this method are poly(4-vinylphenol), poly(3-vinylphenol), poly[(3-vinylphenyl)methanol], poly[2-(4-vinylphenyl)ethanol], poly[2-(3-vinylphenyl)ethanol], and poly[2-(2-vinylphenyl)ethanol].

On the other hand, no appreciable polymerizations take place under exactly the same conditions using *tert*-butyldimethylsilyl ethers of 2-vinylphenol, (4-vinylphenyl)methanol, and (2-vinylphenyl)methanol. These are very structurally similar to the monomers that can produce polymers described above. Thus, the anionic polymerization may clearly be influenced by both the position of the substituent and the number of methylene units separating the silyl group from the phenyl groups. This finding is notable when one attempts to synthesize polystyrenes with hydroxy groups by the method developed here.

References and Notes

(1) Nakahama, S.; Hirao, A. *J. Synth. Org. Chem. Jpn.* **1986**, *44*, 137.

(2) Nakahama, S.; Hirao, A. *Prog. Polym. Sci.* **1990**, *15*, 299.

(3) The recent reports: (a) Suzuki, K.; Yamaguchi, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2607. (b) Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2895. (c) Conlon, D. A.; Crivello, J. V.; Lee, J. L.; O'Brien, M. J. *Macromolecules* **1989**, *22*, 509. (d) Se, K.; Watanabe, O.; Isono, Y.; Fujimoto, T. *Makromol. Chem., Macromol. Symp.* **1989**, *25*, 249. (e) Ishizone, T.; Kato, R.; Ishino, Y.; Hirao, A.; Nakahama, S. *Macromolecules* **1991**, *24*, 1449. (f) Ishizone, T.; Hirao, A.; Nakahama, S.; Kakuchi, T.; Yokota, K.; Tsuda, K. *Macromolecules* **1991**, *24*, 5230.

(4) Hirao, A.; Yamaguchi, K.; Takenaka, K.; Suzuki, K.; Nakahama, S. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 941.

(5) Hirao, A.; Takenaka, K.; Packirisamy, S.; Yamaguchi, K.; Nakahama, S. *Makromol. Chem.* **1985**, *186*, 1157.

(6) Hirao, A.; Takenaka, K.; Yamaguchi, K.; Nakahama, S.; Yamazaki, N. *Polym. Commun.* **1983**, *24*, 339.

(7) Hirao, A.; Yamamoto, A.; Takenaka, K.; Yamaguchi, K.; Nakahama, S. *Polymer* **1987**, *28*, 303.

(8) We previously attempted to polymerize **2a** with either sodium naphthelenide or oligo(α-methylstyryl)disodium. The polymerizations were carried out at -78 °C in THF for 0.5–24 h. **2a** of 5–10 mmol and the initiators of 0.10–0.35 mmol were used. The ratios of [M] to [I] were in the ranges of 20–50. Each of the above experiments was repeated at least once to check the reproducibility of the results. Although the polymerization times varied from 0.5 to 24 h, no polymeric materials could be obtained in all runs.

(9) Ziegler, K.; Dislich, H. *Chem. Ber.* **1957**, *90*, 1107.

(10) Kato, M. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 2175.

(11) Corson, B. B.; Heintzelman, W. J.; Schwartzman, L. H.; Tiefenthal, H. E.; Lokken, R. J.; Nickels, J. E.; Atwood, G. P.; Pavlik, F. J. *J. Org. Chem.* **1958**, *23*, 544.

(12) Dale, W. J.; Starr, L.; Strobel, C. W. *J. Org. Chem.* **1961**, *26*, 2228.

(13) Green, T. W. *Protective Groups in Organic Synthesis*; John Wiley & Sons: New York, 1981; p 44.

(14) Lalonde, M.; Chan, T. H. *Synthesis* **1985**, 817.

(15) Morton, D. R.; Thompson, J. L. *J. Org. Chem.* **1978**, *43*, 2102.

(16) Kende, A. S.; Rizzi, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4247.

(17) Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3688.

(18) Trost, B. M.; Saulnier, M. G. *Tetrahedron Lett.* **1985**, *26*, 123.

(19) Kirk, K. L.; Olubajo, O.; Buchhold, K.; Lewandowski, G. A.; Gusovski, F.; McCulloh, B.; Daly, J. W.; Creveling, C. R. *J. Med. Chem.* **1986**, *29*, 1982.

(20) Okamoto, S.; Kobayashi, Y.; Kato, H.; Hori, K.; Takahashi, T.; Tsuji, J.; Sato, F. *J. Org. Chem.* **1988**, *53*, 5590.

(21) Kuwajima, I.; Takeda, R. *Tetrahedron Lett.* **1981**, *22*, 2381.

(22) Corey, E. J.; Ruker, C. *Tetrahedron Lett.* **1982**, *23*, 719.

(23) Rucker, C. *Tetrahedron Lett.* **1984**, *25*, 4349.

(24) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths Monographs in Chemistry and Chemical Engineering: London, 1981; p 31.

(25) Tuschka, T.; Naito, K.; Rickborn, B. *J. Org. Chem.* **1983**, *48*, 70.

(26) Moss, R. J.; Rickborn, B. *J. Org. Chem.* **1984**, *49*, 3694.

(27) Moss, R. J.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 1992.

(28) Hirao, A.; Kato, K.; Nakahama, S. *Macromolecules* **1992**, *25*, 535.