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Protection and Polymerization of Functional Monomers. 17. Synthesis of Well-Defined Poly(vinylacetophenone)s by Means of Anionic Living Polymerization of *tert*-Butyldimethylsilyl Enol Ethers of Vinylacetophenones

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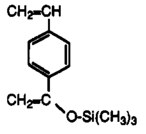
ABSTRACT: The anionic polymerizations of the trimethylsilyl enol ether of 4-vinylacetophenone (**1**), the *tert*-butyldimethylsilyl enol ethers of 4-, 3-, and 2-vinylacetophenones (**2a–c**), the *tert*-butyldimethylsilyl enol ether of 4-vinylpropiophenone (**3**), and the *tert*-butyldimethylsilyl enol ethers of 4-(2-propenyl)acetophenone (**4**), and 4-(2-propenyl)propiophenone (**5**) were carried out in THF at −78 °C with a variety of anionic initiators. Among the monomers, **2a**, **2b**, **3**, **4**, and **5** underwent anionic living polymerization to afford quantitatively polymers of predictable molecular weights from [monomer] to [initiator] ratios and narrow molecular weight distributions. Novel well-defined triblock copolymers of both ABA and BAB types were also synthesized by sequential polymerizations of **2a** or **2b** and styrene and vice versa. On the contrary, attempts to anionically polymerize **1** and **2c** failed under the same conditions. Complete deprotection of the *tert*-butyldimethylsilyl groups of poly(**2a**) and poly(**2b**) to poly(vinylacetophenone)s was achieved by treatment with either 0.5 N HCl or $(C_4H_9)_4NF$. The resulting poly(vinylacetophenone)s were found to possess narrow molecular weight distributions, almost identical to those of the parent poly(**2a**) and poly(**2b**).

Introduction

Recently, we have been developing a new strategy for the synthesis of well-defined functional polymers with regulated polymer chain lengths.[1] The strategy involves the anionic living polymerization of a suitably protected functional monomer, followed by deprotection to regenerate the original functional group. The resulting polymers should have a functional group in all monomer units as well as desirable characteristics of the parent living polymers such as controlled molecular weights and narrow molecular weight distributions.

Through our pioneering work, a variety of polystyrene derivatives with functional groups (OH,[2,3] CH_2CH_2OH,[4,5] NH_2,[6] CH_2NH_2,[7] $CH_2CH_2NH_2$,[7] CHO,[8,9] and COOH[10,11]) as well as poly(2-hydroxyethyl methacrylate)[12] have been successfully synthesized. Others have used a similar strategy for the synthesis of poly(methacrylic acid).[13,14] These polymers all possessed predetermined molecular weights by monomer to initiator ratios and narrow molecular weight distributions. Clearly, this protection–anionic living polymerization–deprotection strategy, if successfully executed, should be quite general and versatile for synthesizing such functional polymers.

As a part of our program to investigate the more general applicability of the above-mentioned strategy, we describe here the synthesis of well-defined poly(vinylacetophenone)s by anionic living polymerization of the protected vinylacetophenones in which the carbonyl groups are protected as silyl enol ether functionalities. The protected monomers employed in this study are the trimethylsilyl enol ether of 4-vinylacetophenone (**1**), the *tert*-butyldimethylsilyl enol ethers of 4-, 3-, and 2-vinylacetophenones (**2a–c**), the *tert*-butyldimethylsilyl enol ether of 4-vinylpropiophenone (**3**), and the *tert*-butyldimethylsilyl enol ethers of 4-(2-propenyl)acetophenone (**4**) and 4-(2-propenyl)propiophenone (**5**).



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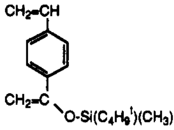

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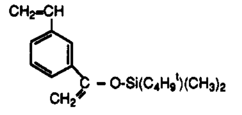

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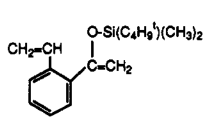

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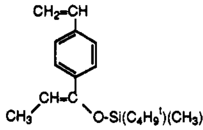

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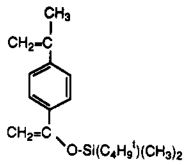

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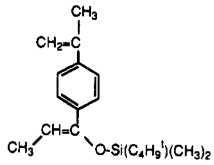

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Experimental Section

Materials. 4-Chlorostyrene (45–46 °C/3 mmHg) and 4-chloro-α-methylstyrene (55–56 °C/3 mmHg) were kindly supplied by Hokko Chemical Industry Co., Ltd. They were distilled over CaH_2 under reduced pressures. Styrene and α-methylstyrene were washed with 5% NaOH and then water. They were dried over $MgSO_4$ and distilled over CaH_2 under a nitrogen atmosphere. After benzylmagnesium chloride (10 mL, 0.25 M in THF solution) was added to styrene or α-methylstyrene (10.0 g), the mixture was degassed and the monomer was distilled together with THF on the vacuum line into an ampule with break-seals, the inside of which was prewashed with sodium naphthalenide in THF. These monomers were diluted with THF and divided into several ampules with break-seals of appropriate amounts. Tetrahydrofuran (THF) was refluxed over sodium wire, distilled from $LiAlH_4$, and finally distilled from its sodium naphthalenide solution on the vacuum line. Naphthalene was purified by

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sublimation. Commercially available *n*-butyllithium (BuLi) was used without purification. Benzylpotassium and cumylpotassium were prepared according to the methods previously reported.[15,16] Their concentrations were determined by the colorimetric titration of bright red solutions to a colorless end point with standardized octanol in sealed reactors with break-seals.[17] Potassium naphthalenide was prepared by the reactions of naphthalene with a small excess of potassium in THF. A characteristic green solution was obtained by filtration, and the concentration was determined by colorimetric titration with standardized octanol. Oligo(α-methylstyryl)lithium and -dipotassium were freshly prepared just prior to the polymerization by the reaction of either BuLi or potassium naphthalenide and a 2–4 M quantity of α-methylstyrene at 25 °C for 0.5 min and then at −78 °C for 15 min. Benzylmagnesium chloride was prepared by the reaction of benzyl chloride with an excess of Mg in THF at 0 °C, and the reaction mixture was stirred at 0 °C for several hours until benzyl chloride disappeared completely. Thus, benzyl chloride free Grignard reagent was obtained and used for purification of monomers.

2-Vinylacetophenone. This compound was synthesized in a manner similar to the previously reported method.[18] The Grignard reagent was prepared by addition of 2-bromostyrene (9.42 g, 51.4 mmol) in THF (50 mL) to Mg (2.43 g, 100 mmol) in THF (10 mL) over a period of 1 h at 0 °C. Stirring was continued for 1 h at room temperature. Then a solution of acetic anhydride (6.26 g, 61.4 mmol) in diethyl ether (50 mL) was added dropwise to the Grignard solution at −78 °C for 1 h. The mixture was stirred at −78 °C for an additional 3 h. It was poured into ice-cold 2 N HCl, extracted twice with ether, washed with 5% NaOH and water, and dried over $MgSO_4$. After evaporation, the remaining pale yellow oil was distilled at 50–53 °C (1 mmHg) to give 6.20 g (42.4 mmol, 83%) of 2-vinylacetophenone as a pale yellow liquid. Greater than 99.5% purity was achieved by fractional distillation (2×): 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.68–7.30 (4 H, m, Ar), 7.21 (1 H, dd, =CH), 5.64, 5.34 (2 H, 2 d, J = 11.0, 17.6 Hz, $CH_2{=}$), 2.58 (3 H, s, CH_3); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 29.8 (CH_3), 116.6 ($CH_2{=}$), 127.5, 128.7, 131.5 (Ar, C3, C4, C5, and C6), 135.9 (=CH), 137.5, 137.7 (Ar C1 and C2; C1 *indicates aromatic carbon bonded to the acetyl group*), 197.8 (C=O).

Similarly, 3-vinyl-, 4-vinyl-, and 4-(2-propenyl)acetophenones were synthesized in good yields from the reactions of 3-bromostyrene, 4-chlorostyrene, and 4-chloro-α-methylstyrene with Mg in THF followed by addition of acetic anhydride in diethyl ether. 3-Vinylacetophenone (55–57 °C/1 mmHg) was obtained in 81% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 8.00–7.33 (4 H, m, Ar), 6.77 (1 H, dd, $CH_2{=}$), 5.82, 5.53 (2 H, 2 d, J = 10.8, 17.6 Hz, =CH), 2.65 (3 H, s, CH_3CO); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 26.5 (CH_3), 115.1 ($CH_2{=}$), 126.0 (Ar, C2), 127.6 (Ar, C6), 130.5 (Ar, C4), 136.0 (=CH), 137.5 (Ar C1), 138.0 (Ar C3), 197.8 (C=O). 4-Vinylacetophenone [63–64 °C/1 mmHg (lit.[19] 80 °C/0.5 mmHg)] was obtained in 68% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.91–7.46 (4 H, m, Ar), 6.75 (1 H, dd, $CH_2{=}$), 5.85, 5.37 (2 H, 2 d, J = 10.8, 17.6 Hz, =CH), 2.58 (3 H, s, CH_3CO); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 26.5 (CH_3), 116.6 ($CH_2{=}$), 126.3 (Ar, C3), 128.7 (Ar, C2), 136.0 (=CH), 136.4 (Ar, C1), 142.1 (Ar, C4), 197.4 (C=O). 4-(2-Propenyl)acetophenone (62–64 °C/0.2 mmHg) was obtained in 62% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.90, 7.51 (4 H, 2 d, J = 8.8 Hz, Ar), 5.45, 5.18 (2 H, 2 s, $CH_2{=}$), 2.57 (3 H, s, CH_3CO), 2.15 (3 H, s, $=CCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 21.5 ($=C\mathit{C}H_3$), 26.4 $\mathit{C}H_3CO$), 114.6 ($=CH_2$) 125.5 (Ar, C3), 128.3 (Ar, C2), 136.0 (Ar, C1), 142.3 ($\mathit{C}{=}CH_2$), 145.7 (Ar, C4), 197.4 (C=O).

4-Vinylpropiophenone and 4-(2-propenyl)propiophenone were synthesized by the reactions of 4-chlorostyrene and 4-chloro-α-methylstyrene with Mg in THF followed by addition of propionic anhydride in diethyl ether. 4-Vinylpropiophenone (75–77 °C/1 mmHg) was obtained in 60% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.89, 7.42 (4 H, 2 d, J = 8.6 Hz, Ar), 6.72 (1 H, dd, =CH), 5.81, 5.34 (2 H, 2 H, 2 d, J = 10.8, 17.6 Hz, $CH_2{=}$), 2.94 (2 H, q, $COC\mathit{H}_2CH_3$), 1.18 (3 H, t, J = 7.2 Hz, CH_3); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 8.2 (CH_3), 31.7 ($\mathit{C}H_2CH_3$), 116.4 ($CH_2{=}$), 126.3 (Ar, C3), 128.3 (Ar, C2), 136.0 (=CH), 136.2 (Ar, C1), 142.9 (Ar, C4), 200.1 (C=O). 4-(2-Propenyl)propiophenone (75–80 °C/1 mmHg) was obtained in 71% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.94, 7.54 (4 H, 2 d, J = 8.4 Hz, Ar), 5.48, 5.20 (2 H, 2 s, $=CH_2$), 3.01 (2 H, q, $C\mathit{H}_2CH_3$), 2.18 (3 H, s, $=CCH_3$), 1.23 (3 H, t, J = 7.3 Hz, $CH_2C\mathit{H}_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 8.4 ($CH_2\mathit{C}H_3$), 21.6 ($=C\mathit{C}H_3$), 31.8 ($\mathit{C}H_2CH_3$), 114.6 ($CH_2{=}$), 125.6 (Ar, C3), 128.1 (Ar, C2), 135.9 (Ar, C1), 142.5 ($\mathit{C}{=}CH_2$), 145.7 (Ar, C4), 200.3 (C=O).

4-[1-((Trimethylsilyl)oxy)ethenyl]styrene (1). The silyl enol ether 1 was prepared from 4-vinylacetophenone, triethylamine, and trimethylsilyl chloride similarly according to the general method of House et al.[20] 1 (59–60 °C/1 mmHg) was obtained in 60% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.54, 7.33 (4 H, 2 d, J = 8.6 Hz, Ar), 6.70 (1 H, dd, =CH), 5.73, 5.22 (2 H, 2 d, J = 10.6, 17.1 Hz, $CH_2{=}$), 4.91, 4.41 (2 H, 2 s, $OC{=}CH_2$), 0.25 (9 H, s, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ 0.17 ($SiCH_3$), 91.2 ($OC\mathit{C}H_2$), 114.0 ($CH_2{=}$), 125.5, 126.0 (Ar, C2, C3), 136.6 (=CH), 137.1, 137.6 (Ar, C1, C4), 155.6 (OC=).

4-[1-((*tert*-Butyldimethylsilyl)oxy)ethenyl]styrene (2a). The silyl enol ether **2a** was synthesized by a method similar to that previously reported by Turner et al.[21] To a stirred suspension of potassium hydride (mineral oil free) (4.13 g, 103 mmol) in dry THF (50 mL) at −78 °C was added dropwise over 30 min 4-vinylacetophenone (5.94 g, 40.6 mmol) in dry THF (30 mL) under an atmosphere of nitrogen. The mixture was stirred for an additional 1 h at −78 °C and then was treated with *tert*-butyldimethylsilyl chloride (7.58 g, 50.3 mmol) in dry THF (60 mL), while rigorous stirring was maintained. The reaction mixture was allowed to warm to room temperature and stirring was continued overnight. After cautious addition of 25 mL of water, the product was extracted with ether three times. The ether layer was washed with saturated NaCl and dried over $MgSO_4$. After filtration and evaporation of the solvent, the residual oil was fractionally distilled under reduced pressure to afford a colorless liquid of desired **2a** (89–91 °C/1 mmHg) in 67% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.56, 7.35 (4 H, 2 d, J = 8.4 Hz, Ar), 6.71 (1 H, dd, =CH), 5.73, 5.23 (2 H, dd, J = 10.8, 17.6 Hz, $CH_2{=}$), 4.88, 4.40 (2 H, 2 s, $OC{=}CH_2$), 0.99 (9 H, s, CCH_3), 0.19 (6 H, s, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ −4.5 ($SiCH_3$), 18.4 ($\mathit{C}CH_3$), 26.0 ($C\mathit{C}H_3$), 91.1 ($OC{=}\mathit{C}H_2$), 114.0 ($CH_2{=}$), 125.6, 126.1 (Ar, C2, C3), 136.6 (=CH), 137.4, 137.6 (Ar, C1, C4), 155.8 (OC=).

Similarly, the silyl enol ethers **2b**, **2c**, **3**, **4**, and **5** were synthesized from the respective ketones. **2b** (72–73 °C/0.25 mmHg) was obtained in 60% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.64–7.31 (4 H, m, Ar), 6.72 (1 H, dd, =CH), 5.74, 5.23 (2 H, 2 d, J = 10.8, 17.1 Hz, $CH_2{=}$), 4.89, 4.41 (2 H, 2 s, $OC{=}CH_2$), 0.99 (s, 9 H, CCH_3), 0.19 (s, 6 H, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ −4.5 ($SiCH_3$), 18.4 ($\mathit{C}CH_3$), 26.0 ($C\mathit{C}H_3$), 91.2 ($OC{=}\mathit{C}H_2$), 114.0 ($CH_2{=}$), 123.3 (Ar, C2), 124.9 (Ar, C6), 126.1 (Ar, C5), 128.3 (Ar, C4), 137.0 (=CH), 137.5 (Ar, C1), 138.2 (Ar, C3), 156.0 (OC=). **2c** (74–76 °C/0.1 mmHg) was obtained in 77% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.56–7.27 (4 H, m, Ar), 7.11 (1 H, 2 d, =CH), 5.65, 5.22 (2 H, 2 d, J = 11.0, 17.6 Hz, $CH_2{=}$), 4.62, 4.43 (2 H, 2 s, $OC{=}CH_2$), 0.90 (9 H, s, CCH_3), 0.08 (6 H, s, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ −4.6 ($SiCH_3$), 18.3 ($\mathit{C}CH_3$), 25.8 ($C\mathit{C}H_3$), 97.0 ($OC{=}\mathit{C}H_2$), 114.2 ($CH_2{=}$), 125.7, 127.3, 128.2, 128.8 (Ar C3–C6), 136.4 (=CH), 136.0, 138.3 (Ar, C1, C2), 156.7 (OC=). **3** (81–84 °C/0.07 mmHg) was obtained in 67% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.40, 7.29 (4 H, 2 d, J = 9.2 Hz, Ar), 6.69 (1 H, dd, =CH), 5.71, 5.20 (2 H, 2 d, J = 10.8, 17.6 Hz, $CH_2{=}$), 5.21 (1 H, q, $CHC\mathit{H}_3$), 1.72 (3 H, d, $C\mathit{H}CH_3$), 0.98 (9 H, s, CCH_3), −0.04 (6 H, s, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ −3.8 ($SiCH_3$), 11.9 ($=CH\mathit{C}H_3$), 18.5 ($\mathit{C}CH_3$), 26.0 ($C\mathit{C}H_3$), 106.0 ($=\mathit{C}HCH_3$), 113.5 ($CH{=}\mathit{C}H_2$), 125.9 (Ar, C2, C3), 136.7 ($\mathit{C}H{=}CH_2$, Ar, C1), 139.4 (Ar, C4), 150.1 (OC=). **4** (77–78 °C/0.25 mmHg) was obtained in 62% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.57, 7.41 (4 H, 2 d, J = 8.6 Hz, Ar), 5.38, 5.08 (2 H, 2 s, $CH_2{=}$), 4.88, 4.40 (2 H, 2 s, $OC{=}CH_2$), 2.14 (3 H, s, $=CCH_3$), 0.99 (9 H, s, CCH_3), 0.19 (6 H, s, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ −4.5 ($SiCH_3$), 18.4 ($\mathit{C}CH_3$), 21.8 ($=C\mathit{C}H_3$), 26.0 ($C\mathit{C}H_3$), 90.9 ($OC{=}\mathit{C}H_2$), 112.5 ($CH_3C{=}\mathit{C}H_2$), 125.2 (Ar, C2, C3), 137.0 (Ar, C4), 141.0 ($CH\mathit{C}{=}CH_2$), 142.9 (Ar, C1), 155.9 (OC=). **5** (86–89 °C/1 mmHg) was obtained in 59% yield: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.37 (4 H, s, Ar), 5.37, 5.05 (2 H, 2 s, $CH_2{=}$), 5.21 (1 H, q, $C\mathit{H}CH_3$), 2.13 (3 H, s, $=CCH_3$), 1.72 (3 H, d, $CHC\mathit{H}_3$), 0.98 (9 H, s, CCH_3), −0.04 (6 H, s, $SiCH_3$); 22.5-MHz ^{13}C NMR ($CDCl_3$) δ −3.8 ($SiCH_3$), 11.9 ($CH\mathit{C}H_3$), 18.5 ($\mathit{C}CH_3$), 21.8 ($=CCH_3$), 26.1 ($C\mathit{C}H_3$), 105.8 ($\mathit{C}HCH_3$), 121.1 ($CH_2{=}$), 125.1, 125.6 (Ar, C2, C3), 139.0 (Ar, C1), 140.1 ($CH_3C{=}CH_2$), 142.9 (Ar, C4), 150.1 (OC=).

NOE measurement of the ^{1}H NMR spectra of **3** and **5** indicates that the thermodynamically more stable Z isomers are formed stereoselectively from both 4-vinylpropiophenone and 4-(2-propenyl)propiophenone.[21,22]

Homopolymerization. All the polymerizations were carried out at −78 °C for 10 min to 96 h with shaking under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with break-seals in the usual manner. The desired charge of monomer in THF solution was added to a THF solution of initiator with strong stirring. Both solutions must be kept at −78 °C. The polymerization was then terminated with degassed methanol at −78 °C. The polymer was precipitated by pouring the mixture into a large amount of methanol. It was purified by two reprecipitations from THF solution to methanol and freeze-dried. The 90-MHz ^{1}H NMR spectra of the resulting polymers in $CDCl_3$ were as follows: Poly(**2a**) δ 7.3–6.4 (4 H, m, Ar), 4.8, 4.3 (2 H, s, $OC{=}CH_2$), 2.3–1.0 (3 H, m, CH_2CH), 0.95 (9 H, s, CCH_3), 0.15 (6 H, s, $SiCH_3$). Poly(**2b**) δ 7.4–6.1 (4 H, m, Ar), 4.55, 4.35 (2 H, s, $OC{=}CH_2$), 2.3–1.0 (3 H, m, CH_2CH), 0.95 (9 H, s, CCH_3), 0.15 (6 H, s, $SiCH_3$). Poly(**3**) δ 7.4–6.1 (4 H, m, Ar), 5.1 (1 H, s, $OC{=}CH$), 2.3–1.0 (3 H, m, CH_2CH), 1.7 (3 H, m, $C{=}CHCH_3$), 0.95 (9 H, s, CCH_3), 0.15 (6 H, s, $SiCH_3$). Poly(**4**) δ 7.9–6.3 (4 H, m, Ar), 4.8, 4.3 (2 H, s, $OC{=}CH_2$), 2.0–1.5 (2 H, m, CH_2C), 1.00 (9 H, s, $SiCCH_3$), 0.20 (3 H, s, CCH_3), 0.10 (6 H, s, $SiCH_3$). Poly(**5**) δ 7.4–6.3 (4 H, m, Ar), 5.1 (1 H, m, $OC{=}CH$), 2.2–1.3 (2 H, m, CH_2C), 1.7 (3 H, m, $C{=}CHCH_3$), 0.95 (9 H, s, CCH_3), −0.10 (3 H, s, CCH_3), −0.15 (6 H, s, $SiCH_3$).

Block Copolymerization. Block copolymerization was carried out in a manner similar to homopolymerization except for the use of two kinds of monomers. Block copolymers of both ABA and BAB types were obtained by sequential addition of A and B monomers (or B and A monomers) in this order to an anionic initiator at −78 °C in THF. Yields were quantitative in all cases. The block copolymers were purified by two reprecipitations from THF to methanol and freeze-dried. They were characterization by IR, ^{1}H and ^{13}C NMR, SEC, and VPO.

Deprotection of the *tert*-Butyldimethylsilyl Groups from Polymers of 2a and 2b. (1) Deprotection with 0.5 N HCl. Poly(**2b**) (0.180 g) was dissolved in THF (5 mL) and cooled at 0 °C. Concentrated HCl (0.2 mL) was added dropwise to the solution, and the mixture was stirred at 25 °C for 1.5 h. The polymer was precipitated by adding the mixture to water and purified by two reprecipitations from THF solution to methanol. The yield of polymer was quantitative (0.102 g, 100%). The polymer was identified as poly(3-vinylacetophenone) by its ^{1}H NMR and IR spectra: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.8–6.2 (4 H, m, Ar), 2.45 (3 H, s, $COCH_3$), 2.2–0.8 (3 H, m, CH_2CH); IR ν 1682 cm^{-1} (C=O).

Similarly, the deprotection reaction of poly(**2a**) was carried out. The yield of polymer was quantitative. The resulting polymer was identified as poly(4-vinylacetophenone) by ^{1}H NMR and IR analyses, respectively: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.9–6.2 (4 H, m, Ar), 2.50 (3 H, s, $COCH_3$), 1.19–1.1 (3 H, m, CH_2CH); IR ν 1681 cm^{-1} (C=O).

(2) Deprotection with $(C_4H_9)_4NF$. Poly(**2b**) (0.214 g) was dissolved in THF (1.5 mL) and cooled at 0 °C. $(C_4H_9)_4NF$ in THF (1.0 M, 1.7 mL) was added dropwise to the solution, and the mixture was stirred at 25 °C for 1 h. The polymer was precipitated by adding the mixture to water and purified by two reprecipitations from THF solution to methanol. The yield of polymer was quantitative (0.121 g, 100%). The polymer was identified as poly(3-vinylacetophenone) by its ^{1}H NMR and IR spectra.

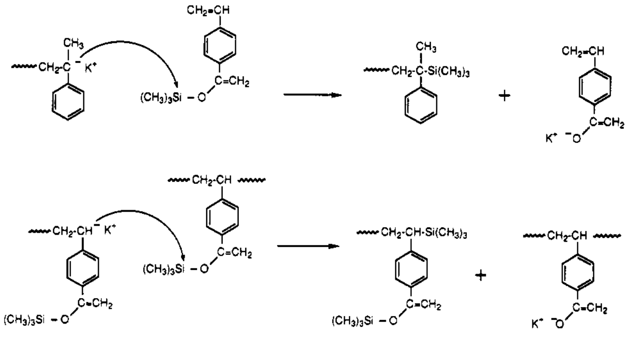
Measurements. Infrared (IR) spectra were recorded on a Jasco IR-G spectrophotometer. ^{1}H NMR and ^{13}NMR spectra were recorded on a JEOL FX-90Q in $CDCl_3$. Chemical shifts are reported in ppm downfield relative to $(CH_3)_4Si$ (δ 0) for ^{1}H NMR and $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Size exclusion chromatograms (SEC) for characterization of molecular weight distributions were obtained at 40 °C with a Toyo Soda HLC-802 instrument with ultraviolet or refractive index detection (polyethylene standard). THF was the carrier solvent at a flow rate of 1.4 mL/min. Vapor pressure osmometry (VPO) measurements for $\bar{M}_n$ determination were made with a Corona 117 instrument in benzene solutions with a highly sensitive thermoelectric couple and equipment of very exact temperature control. Therefore, molecular weights up to 10^5 could be determined within an analytical error of ±5%.

Results and Discussion

Although a variety of carbonyl protecting groups could be envisaged, we felt that a silyl enol ether functionality might be a good choice for our purpose. Silyl enol ethers are generally prepared from the parent ketones in good yields by well-established methods.[20,21,23–26] They are sufficiently stable to permit isolation but can be conveniently deprotected to regenerate the corresponding ketones under mild reaction conditions. More importantly, previous works by Piers et al.,[27] Kuwajima et al.,[28] and Trimitsis et al.[29] have demonstrated that the certain silyl enol ethers can survive a variety of lithiation conditions very similar to those of anionic living polymerization of styrene derivatives. In view of these findings, the protection of the carbonyl groups of vinylacetophenones and anionic polymerization of the protected monomers might be possible.

Anionic Polymerizations of Silyl Enol Ether Substituted Styrene Derivatives 1–5. The trimethylsilyl enol ether of 4-vinylacetophenone (**1**) was employed as the first example of a protected monomer. The polymerization was carried out in THF at −78 °C with oligo(α-methylstyryl)dipotassium. However, it was found that no appreciable polymerization occurred in this system. Termination is obviously rapid since the characteristic dark red color of oligo(α-methylstyryl)dipotassium disappears instantaneously upon monomer addition. In fact, no polymeric material was obtained. Thus, the protection by trimethylsilyl enol ether failed in the case of 4-vinylacetophenone under a typical condition of anionic polymerization as above.

It is known that trimethylsilyl enol ethers are not very stable under strongly basic conditions. For example, the addition of alkyllithium (RLi) to trimethylsilyl enol ethers generally transforms them into lithium enolates by nucleophilic attack of RLi at the silicon atom.[24,30–32] Accordingly, a similar reaction may possibly take place to terminate the polymerization of **1** at the initiation step and/or early stage of the polymerization as shown below:



The difficulty of polymerization was overcome by using the more bulky *tert*-butyldimethylsilyl group to protect the carbonyl function of 4-vinylacetophenone. Reaction of 4-vinylacetophenone with potassium hydride afforded the corresponding enolate, which upon treatment with *tert*-butyldimethylsilyl chloride gave the expected **2a**. The polymerization of **2a** was carried out in THF at −78 °C with oligo(α-methylstyryl)dipotassium. Upon addition of **2a** to the initiator solution, an immediate and characteristic color change from dark red to dark reddish brown occurred. The color remained unchanged at −78 °C after 24 h but gradually faded at 25 °C. It disappeared completely at 25 °C after 2 h. The yield of polymer was always quantitative. The ^{1}H NMR spectrum showed the purified polymer

Table I
Anionic Polymerization of 2a with Oligo(α-methylstyryl)dipotassium in THF at −78 °C for 0.5 h

2a, mmol	K-Nap,[a] mmol	α-MeSt,[b] mmol	$10^{-3}\bar{M}_n$ (calcd)	$10^{-3}\bar{M}_n$ (obsd)[c]	$\bar{M}_w/\bar{M}_n$[d]
2.75	0.144	0.404	11	9.5	1.08
2.57	0.0958	0.304	15	13	1.06
2.32	0.638	0.215	20	18	1.06
2.75	0.0391	0.197	38	39	1.08

[a] Potassium naphthalenide. [b] α-Methylstyrene. [c] $\bar{M}_n$(obsd) was measured by VPO in benzene solution. The values of $\bar{M}_n$(GPC) were 8 300, 11 000, 15 000, and 33 000 based on a standard polystyrene calibration. [d] $\bar{M}_w/\bar{M}_n$ was determined from a SEC profile based on a standard polystyrene calibration.

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

2b,	initiator		α-MeSt,[a]	$10^{-3}\bar{M}_n$-	$10^{-3}\bar{M}_n$-	
mmol		mmol	mmol	(calcd)	(obsd)	$\bar{M}_w/\bar{M}_n$[c]
2.07	K-Nap[d]	0.0841	0.326	14	13	1.06
3.95	K-Nap	0.100	0.107	21	19	1.06
4.54	K-Nap	0.0752	0.347	33	27	1.06
7.03	cumyl K[e]	0.0371		49	54	1.05
3.21	BuLi[f]	0.080	0.325	11	11	1.04

[a] α-Methylstyrene. [b] $\bar{M}_n$(obsd) was measured by VPO. The values of $\bar{M}_n$(GPC) were 12 000, 19 000, 25 000, 49 000, and 10 000 for five samples. [c] $\bar{M}_w/\bar{M}_n$ was determined from a SEC profile based on a standard polystyrene calibration. [d] Potassium naphthalenide. [e] Cumylpotassium. [f] Butyllithium.

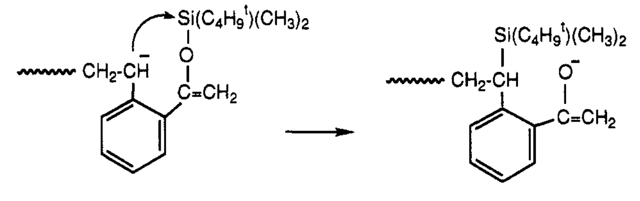
sample to be poly(**2a**) with virtually no cleavage of the silicon–oxygen bond.

The results are summarized in Table I, which includes the $\bar{M}_n$ values observed and calculated from monomer to initiator ratios and the $\bar{M}_w/\bar{M}_n$ values as polydispersity index. A comparison of the four molecular weights for each polymer showed that the $\bar{M}_n$ values observed were in fair agreement with those calculated. The nearly monodisperse character of these samples was confirmed by their SEC profiles of sharp and single peaks. The $\bar{M}_w/\bar{M}_n$ values were less than 1.1 in all cases. These results, in addition to the observation of the coloration in the polymerization system, are consistent with the "living" character of the polymerization of **2a**. Obviously, the *tert*-butyldimethylsilyl enol ether in **2a** is sufficiently stable under the conditions of polymerization where the trimethylsilyl counterpart, **1**, is destroyed. Thus, the *tert*-butyldimethylsilyl enol ether functionality satisfactorily protects the carbonyl group of 4-vinylacetophenone.

Similarly, the metal isomer, **2b**, was found to undergo anionic living polymerization. A characteristic dark reddish brown color in the system again indicates the presence of a carbanion derived from **2b**. The yields of polymers were quantitative in all cases. As seen from Table II, good agreement between the observed and calculated $\bar{M}_n$ values and narrow distributions of molecular weight were realized in all the polymer samples initiated with oligo(α-methylstyryl)dipotassium. Oligo(α-methylstyryl)lithium and cumylpotassium were also found to be effective initiators.

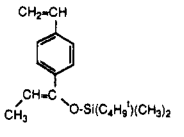
On the contrary, attempts to anionically polymerize the ortho isomer, **2c**, failed with oligo(α-methylstyryl)dipotassium and -dilithium in THF at −78 °C. The characteristic dark red colors of the initiators faded completely to pale brown in these systems. No polymers were obtained, and instead, most of the starting **2c** was recovered in both cases. This is in marked contrast to the fact that the para and meta derivatives, **2a** and **2b**, polymerize well to afford "living polymers".

As mentioned before, trimethylsilyl enol ethers are not stable in the presence of carbanionic species and readily react with them to afford the enolate anions. On the other hand, *tert*-butyldimethylsilyl enol ethers have been reported to be stable under the same conditions.[27-29] In fact, the stability is clear from the fact that they work well as protective groups in the anionic polymerizations of **2a** and **2b**. However, it has been reported that even *tert*-butyldimethylsilyl enol ethers and the bulkier triisopropylsilyl analogue are intramolecularly attacked by carbanions in the cases where they are present at certain special positions. Anionic 1,3 O → C[33,34] and 1,4 O → C[35] silyl rearrangements are the typical examples. Therefore, in view of these results, the difficulty in the polymerization of **2c** may possibly be explained by the intramolecular reaction of *tert*-butyldimethylsilyl enol ether in the ortho position with initiator and/or the carbanions made by a subsequent propagation reaction. A plausible mechanism for the termination reaction is shown below:

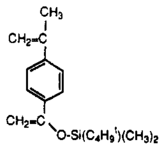


Whatever the reason, attention should be called to the use of ortho-substituted styrenes with silyl enol ether functions in anionic polymerization.

We also examined a couple of minor variations of monomer structure to ascertain whether *tert*-butyldimethylsilyl enol ether was generally effective for protection of the carbonyl groups of styrene derivatives. The following three monomers were synthesized and used for this purpose:



3



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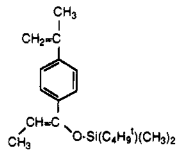


5

The polymerizations of **3**, **4**, and **5** were carried out at −78 °C in THF with potassium naphthalenide, oligo(α-methylstyryl)dipotassium, benzylpotassium, or cumylpotassium as initiator. The polymerization mixtures exhibited characteristic reddish brown colors in all runs which disappeared immediately upon addition of a few drops of methanol. Under the conditions employed, the polymerization of **3** was very fast and complete within a few minutes. On the other hand, the α-methylstyrene analogues, **4** and **5**, underwent polymerization at slow rates. The polymerizations required 24–96 h for quantitative conversion. Typical results are summarized in Table III.

It may be seen from Table III that there is good agreement between the observed and calculated values of $\bar{M}_n$ in all runs. A narrow molecular weight distribution was also observed in each of these polymer samples. It is apparent from these results that the polymerizations of **3**–**5** proceed without chain termination reactions to give living polymers. Thus, the protection by *tert*-butyldimethylsilyl enol ether is also effective for the propiophenone derivatives, **3** and **5**, and the α-methylstyrene analogues, **4** and **5**, are found to undergo anionic living polymerization without difficulty.

Block Copolymerization. The living character of polymerization provides the best method for synthesizing block copolymers in which each block has a predictable molecular weight and a very narrow molecular weight

Table III
Anionic Polymerizations of 3, 4, and 5 in THF at −78 °C[a]

monomer		initiator						
	mmol		mmol	α-MeSt,[b] mmol	time, h	$10^{-3}\bar{M}_n$(calcd)	$10^{-3}\bar{M}_n$(obsd)	$\bar{M}_w/\bar{M}_n$[d]
3	2.53	K-Nap[e]	0.115	0.407	0.5	13	11	1.05
3	2.77	K-Nap	0.0999	0.389	0.5	16	14	1.10
4	2.41	cumyl K[f]	0.0558		48	12	12	1.02
4	2.81	benzyl K[g]	0.0590		96	13	11	1.03
5	2.30	K-Nap	0.132	0.349	24	10	11	1.06
5	2.96	K-Nap	0.119		24	14	12	1.04

[a] Yields of polymers were 100% in all runs. [b] α-Methylstyrene. [c] $\bar{M}_n$(obsd) was measured by VPO. The values of $\bar{M}_n$(GPC) were 9 200, 11 000, 9 700, 8 900, 9 400, and 5 200 based on a standard polystyrene calibration. [d] $\bar{M}_w/\bar{M}_n$ was determined from a SEC profile based on a standard polystyrene calibration. [e] Potassium naphthalenide. [f] Cumylpotassium. [g] Benzylpotassium.

Table IV
Block Copolymerization of 2a or 2b with Styrene in THF at −78 °C[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]	$\bar{M}_n/\bar{M}_n$[e]
A-B-A	**2a**	styrene	25 (10)	27 (11)	1.05
B-A-B	**2a**	styrene	26 (9.4)	28 (9.5)	1.11
A-B-A	**2b**	styrene	30 (15)	31 (15)	1.05
B-A-B	**2b**	styrene	30 (11)	30 (11)	1.05

[a] Oligo(α-methylstyryl)dipotassium was used. Yields of polymers were 100% in all runs. [b] Polymerization times at the first and at the second stages were 0.5 and 0.5 h, respectively. [c] Homopolymers were obtained at the first-stage polymerization. [d] $\bar{M}_n$(obsd) was measured by VPO. [e] $\bar{M}_w/\bar{M}_n$ was determined from a SEC profile based on a standard polystyrene calibration.

distribution. With the use of the living polymers of **2a** and **2b**, we have attempted to synthesize such well-defined block copolymers. The synthesis of a B–A–B triblock copolymer was carried out by addition of styrene as monomer B to the living polymer of either **2a** or **2b**. In both cases, the yields of polymers were quantitative based on the monomer weights used. The results of block copolymerizations are summarized in Table IV. The observed $\bar{M}_n$ values by VPO and compositions of the resulting polymers were found to be almost equal to those calculated from monomer ratios and ^{1}H NMR measurements. The SEC profiles showed that the polymers possessed narrow molecular weight distributions. Furthermore, these peaks were almost symmetrical without any significant amounts of low and high molecular weight materials. Thus, well-defined block copolymers of both poly(styrene-*b*-**2a**-*b*-styrene) and poly(styrene-*b*-**2b**-*b*-styrene) were successfully synthesized. The results also provide a strong and direct evidence of the living character in the polymerizations of **2a** and **2b**.

Similarly, the A–B–A triblock copolymers with reverse sequences were quantitatively synthesized by addition of either **2a** or **2b** to living polystyrene. Both poly(**2a**-*b*-styrene-*b*-**2a**) and poly(**2b**-*b*-styrene-*b*-**2b**) thus obtained were also found to have predictable $\bar{M}_n$ values, compositions, and narrow molecular weight distributions, as shown in Table IV.

It is possible to estimate the stability of living polymer by the analyses of molecular weights and their distributions of the polymers obtained by block copolymerization. The following experiments were carried out to evaluate the stability of living polymers of **2a** and **2b**. The living polymer of either **2a** or **2b** was prepared in THF at −78 °C for 0.5 h and then allowed to stand at the same temperature for an additional 24 h. Then the addition of styrene resulted in quantitative formation of the desired B–A–B triblock copolymers in the cases of both **2a** and **2b**. This indicates that the living polymers of **2a** and **2b** are sufficiently stable at −78 °C after 24 h.

On the other hand, it was found that the living polymers of **2a** and **2b** were predominantly deactivated at 25 °C even after 1 h. For example, **2a** was polymerized at −78 °C for 0.5 h and then the polymerization mixture was allowed to stand at 25 °C for 1 h. After the mixture was again cooled at −78 °C, the addition to styrene resulted in the formation of a block copolymer of very high molecular weight ($\bar{M}_n$(obsd) = 300 000) together with recovery of the starting homopolymer of **2a**. From the SEC analysis it can be concluded that about 90% of the living poly(**2a**) was already deactivated before addition of styrene to the system. Under the same conditions, no block copolymer was obtained at all in the case of **2b**. The starting homopoly(**2b**) and styrene were recovered quantitatively, indicating that the living polymer of **2b** was completely deactivated at 25 °C after 1 h. According, the living polymers of **2a** and **2b** proved to be stable at −78 °C but quite unstable at 25 °C. Thus, the effect of temperature was quite distinct on the stability of living polymers of **2a** and **2b**.

Deprotection of the *tert*-Butyldimethylsilyl Group from Polymers of 2a and 2b. As mentioned in the preceding section, the *tert*-butyldimethylsilyl enol ether functions of poly(**2a**) and poly(**2b**) stayed intact during the polymer purification step. No cleavage of the silyl functionality was also found in an aqueous THF solution under neutral conditions. Therefore, polymers of **2a** and **2b** were isolated without difficulty and were used in these forms for characterization by VPO, NMR, IR, ^{1}H NMR, and ^{13}C NMR analyses.

On the contrary to the stability of polymer under neutral conditions, it was found that the silyl enol ether functions of polymers could be readily and completely converted into the corresponding ketones by treating with either 0.5 N HCl or $(C_4H_9)_4NF$ in a manner similar to that previously reported for the low molecular weight analogues. For example, poly(**2b**) was treated with 0.5 N HCl in a THF–H_2O mixture (12/1, v/v) at 25 °C for 1.5 h. The mixture was precipitated from water. It was purified by two reprecipitations from THF to methanol. The yield of polymer isolated was 100% assuming complete conversion to poly(3-vinylacetophenone).

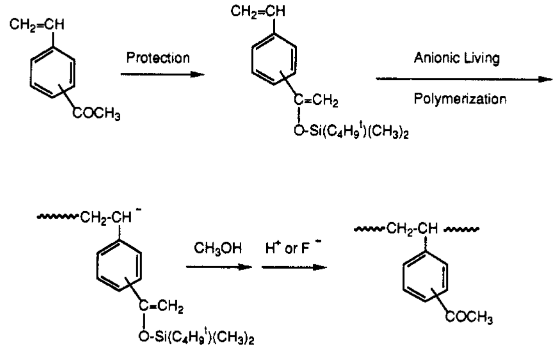
The IR spectrum of the resulting polymer exhibited a new strong band at 1682 cm^{-1} characteristic for a carbonyl group and complete disappearance of the absorptions at 1010, 1110, and 1257 cm^{-1} due to Si–O–C stretching and Si–CH_3 deformation vibrations and at 839 and 1619 cm^{-1} due to C=C stretching and C–H deformation vibrations of the silyl enol ether. The ^{1}H NMR spectrum was also consistent with the assigned structure of poly(3-vinylacetophenone). The signal for the acetyl protons appeared at 2.45 ppm, whereas no trace of the signals at 0.15 and 0.95 ppm corresponding to the methyl protons of the *tert*-butyl and methylsilyl groups could be detected. It was found that the integral ratio of acetyl to aromatic protons was exactly 3:4 as expected. The same analytical result was also obtained by ^{13}C NMR. These results reveal that complete deprotonation can be achieved under the conditions employed.

The SEC profile of this resulting polymer showed that the sample still possessed a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.05$) and eluted in a reasonable molecular region. This indicates no detectable side reactions leading to main-chain degradation and/or chain branching during the deprotection step.

Similarly, treatment of poly(**2a**) with 0.5 N HCl led to poly(4-vinylacetophenone) quantitatively without side reactions. Under the same conditions, the silyl enol ether function of the block copolymers was also successfully deprotected to afford novel block copolymers having poly(**2a**) or poly(**2b**) segments.

The complete conversion of poly(**2b**) to poly(3-vinylacetophenone) was similarly achieved by treating it with $(C_4H_9)_4NF$ in THF at 25 °C for 1 h. Again the molecular weight distribution was unchanged, indicating no side reactions under the above conditions. This deprotection method using $(C_4H_9)_4NF$ is especially attractive because the reaction can be run in a variety of nonaqueous media under nearly neutral conditions.

In summary, it is demonstrated that the successful overall transformation of 3(or 4)-vinylacetophenone to the corresponding well-defined polymers, via protection and anionic living polymerization, is realized as shown below. Unfortunately, this transformation cannot be applied to 2-vinylacetophenone.



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Registry No. 1, 137494-46-3; **2a**, 137494-47-4; **2a** (homopolymer), 137494-54-3; (**2a**)(St) (block copolymer), 137494-61-2; **2b**, 137494-48-5; **2b** (homopolymer), 137494-55-4; (**2b**)(St) (block copolymer), 137494-60-1; **2c**, 137494-49-6; **3**, 137494-50-9; **3** (homopolymer), 137494-56-5; **4**, 129181-43-7; **4** (homopolymer), 137494-58-7; **5**, 137494-51-0; **5** (homopolymer), 137494-59-8; 2-vinylacetophenone, 52095-40-6; 2-bromostyrene, 2039-88-5; acetic anhydride, 108-24-7; 3-bromostyrene, 2039-86-3; 4-chlorostyrene, 1073-67-2; 4-chloro-α-methylstyrene, 1712-70-5; 3-vinylacetophenone, 64217-99-8; 4-vinylacetophenone, 10537-63-0; 4-(2-propenyl)acetophenone, 5359-04-6; propionic anhydride, 123-62-6; 4-vinylpropiophenone, 7646-72-2; 2-(2-propenyl)propiophenone, 137515-51-6; trimethylsilyl chloride, 75-77-4; *tert*-butyldimethylsilyl chloride, 18162-48-6; oligo(α-methylstyryl)dipotassium, 88384-52-5; potassium naphthalenide, 4216-48-2; cumylpotassium, 3003-91-6; butyllithium, 109-72-8; benzylpotassium, 2785-29-7.