Macromolecules 1991, *24*, 1449–1454

Protection and Polymerization of Functional Monomers. 15. Anionic Living Polymerizations of 2-(3-Vinylphenyl)-1,3-dioxolane and Related Monomers

Takashi Ishizone, Ryohei Kato, Yoshiaki Ishino, Akira Hirao,* and Seiichi Nakahama*

Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152, Japan

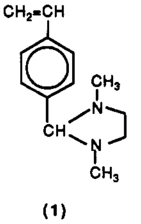
Received May 29, 1990; Revised Manuscript Received October 5, 1990

ABSTRACT: Anionic polymerizations of the three acetal-protected styrene derivatives 2-(2-vinylphenyl)- (**3a**), 2-(3-vinylphenyl)- (**3b**), and 2-(4-vinylphenyl)-1,3-dioxolanes (**3c**) were carried out in THF at −78 °C with a variety of initiators. The meta isomeric monomer, **3b**, underwent anionic living polymerization to produce polymers of controlled molecular weights and narrow molecular weight distributions. New well-defined block copolymers of both the ABA and the BAB types were readily synthesized by the sequential polymerizations of **3b** and styrene and vice versa. On the contrary, complications were observed in the polymerizations of the ortho and para isomers, **3a** and **3c**. Soluble polymers with very broad molecular weight distributions from **3a** and insoluble polymers from **3c** were obtained in low yields by these polymerizations. Thus, the anionic polymerization behavior was significantly influenced by the difference in placement of the acetal group on the aromatic ring of the monomer. To explain these results, we propose a reaction mechanism based on the base-induced 1,6(or 1,4)-elimination of the acetal to generate the very reactive *p*(or *o*)-xylene intermediate. This is the first clear example that shows the positional effect of this substituent in the anionic polymerization of styrene derivatives. The anionic polymerizations of some related styrene derivatives containing acetal functionalities are also described.

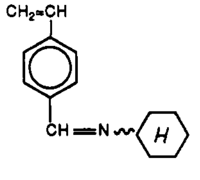
Introduction

Recently, we have been developing the anionic living polymerizations of a series of suitably protected functional monomers, followed by deprotection to regenerate the original functional groups.[1] The resulting polymers had functional groups in each monomer unit as well as the desirable characteristics of the parent living polymers, i.e., controlled molecular weights and narrow molecular weight distributions. Therefore, this protection–anionic living polymerization–deprotection strategy provides a general and valuable route for synthesizing well-defined functional polymers.

In previous papers,[2,3] we reported the successful synthesis of well-defined poly(4-vinylbenzaldehydes) with respect to chain lengths and the block copolymers having these polymer sequences. Our approach to the synthesis of such polymers involves the anionic living polymerizations of both protected monomers, 1,3-dimethyl-2-(4-vinylphenyl)imidazolidine (1)[2] and *N*-[(4-vinylphenyl)-methylene]cyclohexamine (2),[3] followed by the removal of these protecting groups from the resulting polymers. In fact, poly(4-vinylbenzaldehydes) of predictable molecular weights and narrow molecular weight distributions were quantitatively obtained by the above-mentioned methods.

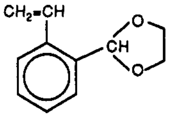


(1)

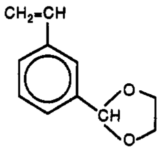


(2)

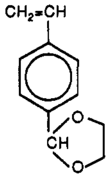
During these studies, we also prepared monomer **3c**, in which the formyl group of 4-vinylbenzaldehyde was protected as its cyclic acetal form (the 1,3-dioxolane ring). As is well-known, acyclic and cyclic acetals are the most widely used protecting groups for the aldehyde function.[4] They are stable to highly reactive basic and nucleophilic reagents often used as anionic initiators but are readily cleaved under mildly acidic conditions. Thus, **3c** seems to be a suitable monomer candidate in the synthetic sequence developed by us which includes an anionic living polymerization step. Unexpectedly, attempts to polymerize **3c** anionically failed, giving only small amounts of insoluble products along with most of the starting monomer. On the other hand, it was found that the meta isomeric monomer (**3b**) underwent anionic living polymerization without difficulty. Thus, the behavior of **3b** and **3c** appears to be completely different in their anionic polymerizations. However, we cannot determine from these results whether the 1,3-dioxolane ring is effective for the protection of the formyl group in the anionic living polymerization.



(3a)

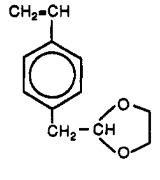


(3b)



(3c)

The ready conversion of aldehyde to the acetal function and the different behavior of **3b** and **3c** in the polymerization led us to examine in more detail the possibility of acetal protection in our synthetic sequence. The acetal-protected monomers **3b** and **3c** in addition to the ortho isomeric monomer **3a** and the related monomer **4** will be prepared and tested for anionic polymerizability.



(4)

0024-9297/91/2224-1449$02.50/0

Experimental Section

Materials. 4-Chlorostyrene was kindly supplied by Hokko Chemical Industry Co., Ltd. It was distilled at 52–54 °C (5 mmHg) over CaH_2 under a nitrogen atmosphere. 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. Benzylmagnesium chloride (10 mL, 0.25 M in THF solution) was added to styrene or α-methylstyrene (10.0 g) and then degassed and distilled on a vacuum line into an ampule with breakseals, the inside of which was prewashed with sodium naphthalenide in THF. These monomers were diluted with THF and divided into several ampules with breakseals of appropriate amounts. Tetrahydrofuran (THF) was refluxed over sodium wire and distilled over $LiAlH_4$. It was then distilled from its sodium naphthalenide solution on a 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 Na–K alloy in THF according to the previous method.[5] The concentration was determined by the colorimetric titration of a bright red solution to a colorless end point with standardized octanol in a sealed reactor with breakseals.[6] Metal naphthalenides were prepared by the reactions of naphthalene with a small excess of the corresponding alkali metal in THF. The characteristic green solutions were obtained by filtration, and their concentrations were determined by colorimetric titration with standardized octanol. Oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium were freshly prepared just prior to the polymerization from the corresponding metal naphthalenides and a 2–4 M quantity of α-methylstyrene at 30 °C for 1 min and then at −78 °C for 10 min. Similarly, oligo(α-methylstyryl)lithium and -potassium were prepared from butyllithium and cumylpotassium and α-methylstyrene. Phenylmagnesium chloride was prepared by the reaction of chlorobenzene with an excess of Mg in THF at a reflux temperature. Complete disappearance of chlorobenzene was checked by gas chromatography. Benzylmagnesium chloride was prepared by the reaction of benzyl chloride with an excess of Mg in THF at 0 °C. Benzyl chloride was found to be completely reacted by gas chromatography.

2-Vinylbenzaldehyde. 2-Vinylbenzaldehyde was synthesized according to the previously reported method.[7] The Grignard reagent was prepared by addition of 2-vinylphenyl bromide (18.3 g, 100 mmol) in THF (50 mL) to Mg (3.55 g, 150 mmol) in THF (100 mL) over 1 h at 0 °C. Stirring was continued for 1 h at room temperature. Then a solution of *N,N*-dimethylformamide (10.0 g, 137 mmol) in THF (50 mL) was added dropwise to the Grignard solution at 0 °C. The mixture was allowed to stand overnight at room temperature. It was then poured into ice-cold saturated NH_4Cl, extracted twice with ether, washed with water, and dried over $MgSO_4$. After 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. A purity of >99.5% was achieved after two fractional distillations. Similarly, 3- and 4-vinylbenzaldehydes were prepared in good yields (70–85%) from the reactions of 3-vinylphenyl bromide and 4-vinylphenyl chloride with *N,N*-dimethylformamide in THF.

2-(2-Vinylphenyl)-1,3-dioxolane (3a). The reaction was performed according to the previously reported method.[8] A solution of 2-vinylbenzaldehyde (5.09 g, 38.6 mmol), ethylene glycol (4.17 g, 67.3 mmol), *p*-toluenesulfonic acid (5 mg), and *tert*-butylcatecohol (1 mg) in benzene (100 mL) was heated at reflux with azeotropic removal of water for 2 h. The solution was washed with 10% $NaHCO_3$ three times and water twice. The benzene layer was dried over $MgSO_4$. Filtration and evaporation gave a pale yellow oil, which was purified by fractional distillation at 95–97 °C (2 mmHg) to give 5.14 g (29.2 mmol, 76%) of **3a** as a colorless liquid: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.64–6.99 (4 H, m, Ar), 7.15 (1 H, dd, J = 17.0, 11.0 Hz, CH=), 6.02 (1 H, s, CHO), 5.68, 5.34 (2 H, dd, J = 17.0, 11.0 Hz, CH_2=), 4.08 (4 H, m, CH_2CH_2); 23-MHz ^{13}C NMR ($CDCl_3$) δ 65.2 (CH_2CH_2), 101.6 (CHO), 116.4 (CH_2=), 125.9, 126.0, 127.5, 129.1 (Ar, primary), 133.9 (CH=), 134.4, 137.0 (Ar, tertiary).

2-(3-Vinylphenyl)-1,3-dioxolane (3b). **3b** was obtained by the reaction of 3-vinylbenzaldehyde (6.40 g, 48.5 mmol) with ethylene glycol (4.00 g, 64.5 mmol) by a method similar to that for **3a**. It was purified by repeated fractional distillation at 73–75 °C (1 mmHg) to give 5.20 g (29.5 mmol, 61%) of **3b** as a colorless liquid: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.41 (4 H, m, Ar), 6.73 (1 H, dd, J = 17.8, 10.8 Hz, CH=), 5.80 (1 H, s, CHO), 5.75, 5.25 (2 H, dd, J = 17.8, 10.8 Hz, CH_2=), 4.07 (4 H, m, CH_2CH_2). Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.00; H, 6.82. Found: C, 74.85; H, 6.94.

2-(4-Vinylphenyl)-1,3-dioxolane (3c). **3c** was obtained by the reaction of 4-vinylbenzaldehyde (7.10 g, 53.8 mmol) with ethylene glycol (3.80 g, 61.3 mmol) by a method similar to that for **3a**. It was purified by repeated fractional distillation at 76–77 °C (0.5–1.0 mmHg) to give 4.05 g (23.0 mmol, 44%) of **3c** as a colorless liquid: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.41 (4 H, m, Ar), 6.71 (1 H, dd, J = 10.8, 17.7 Hz, CH=), 5.78 (1 H, s, CHO), 5.74, 5.24 (2 H, dd, J = 17.8, 10.8 Hz, CH_2=), 4.02 (4 H, m, CH_2CH_2); 23-MHz ^{13}C NMR ($CDCl_3$) δ 65.2 (CH_2CH_2), 103.4 (CHO), 114.3 (CH_2=), 126.1, 126.6 (Ar C2 or C3), 136.4 (CH=), 137.4, 138.4 (Ar, C1 or C4).

(4-Vinylphenyl)acetaldehyde. (4-Vinylphenyl)acetaldehyde was prepared according to the method previously reported by Olah et al.[9] A solution of *N*-formylmorpholine (16.31 g, 142 mmol) in dry diethyl ether (150 mL) was added dropwise at 0 °C to a diethyl ether solution of the Grignard reagent prepared from 4-vinylbenzyl chloride (20.02 g, 131 mmol) and Mg (4.85 g, 200 mmol) in diethyl ether (150 mL). The mixture was stirred at 0 °C for 2 h under a nitrogen atmosphere. The usual workup followed by fractional distillation at 75–77 °C (1 mmHg) (lit.[9] 76–79 °C (10 mmHg)) gave 4.87 g (36.9 mmol, 28%) of pure (4-vinylphenyl)acetaldehyde as a pale yellow liquid. It should be noted that this aldehyde was not stable and on standing became a white solid which could not be distilled.

2-((4-Vinylphenyl)methyl)-1,3-dioxolane (4). A solution of (4-vinylphenyl)acetaldehyde (4.87 g, 36.9 mmol), ethylene glycol (4.04 g, 65.2 mmol), *p*-toluenesulfonic acid (5 mg), and *tert*-butylcatechol (1 mg) in benzene (100 mL) was heated at reflux with azeotropic removal of water for 2.5 h.[8] The solution was washed with 10% $NaHCO_3$, water, and 10% $NaHSO_3$, and the benzene layer was dried over $MgSO_4$. Filtration and evaporation gave a pale yellow oil, which solidified on standing. Recrystallization from hexane provided 4.66 g (24.5 mmol, 66%) of **4** as white needles: mp 24.5 °C; 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.31 (4 H, m, Ar), 6.70 (1 H, dd, J = 10.6, 17.5 Hz, CH=), 5.70, 5.20 (2 H, dd, J = 17.6, 10.8 Hz, CH_2=), 5.05 (1 H, t, J = 4.7 Hz, CHO), 3.94 (4 H, m, CH_2CH_2), 2.95 (1 H, d, J = 4.6 Hz, CH_2). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37. Found: C, 75.38; H, 7.53.

2-(4-Vinylphenyl)-1,3-dioxane (5). A solution of 4-vinylbenzaldehyde (6.60 g, 50 mmol), 1,3-propanediol (5.70 g, 75 mmol), *p*-toluenesulfonic acid (10 mg), and *tert*-butylcatechol (1 mg) in benzene (100 mL) was heated at reflux with azeotropic removal of water for 5 h.[8] The solution was washed with 10% $NaHCO_3$ and water and then dried over $MgSO_4$. Filtration and evaporation gave a pale yellow oil, which was purified by fractional distillation at 88–90 °C (1 mmHg). A total of 7.60 g (40 mmol, 80%) of **5** was obtained as a colorless liquid: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.42 (4 H, d, J = 1.3 Hz, Ar), 6.70 (1 H, dd, J = 10.8 Hz, =CH), 5.95, 5.80 (1 H, s, s, CHO), 5.75, 5.26 (2 H, dd, J = 17.7, 10.8 Hz, CH_2=), 4.25 (2 H, m, OCH_2), 3.60, 1.37 (2 H, m, OCH_2), 1.37 (2 H, m, $CH_2CH_2CH_2$); 23-MHz ^{13}C NMR ($CDCl_3$) δ 18.3, 18.6 ($CH_2CH_2CH_2$), 71.3, 72.0, 72.3, 73.4 (OCH_2), 102.8, 103.8 (CHO), 114.3 (CH_2=), 126.1, 126.8 (Ar, C2 or C3), 136.5 (CH=), 137.5, 138.5 (Ar, C1 or C4).

(4-Vinylphenyl)diethoxymethane (6). The reaction was modified according to the previous method.[10] A mixture of 4-vinylbenzaldehyde (7.50 g, 57 mmol), triethyl orthoformate (9.50 g, 64 mmol), dry ethanol (8.00 g, 173 mmol), and ammonium chloride (0.12 g, 2.3 mmol) was heated at reflux for 20 min. After evaporation of ethanol and triethyl orthoformate, the residual oil was dissolved in diethyl ether. The solution was washed with water and dried over $MgSO_4$. Evaporation and distillation at 77–78 °C (2 mmHg) gave 8.94 g (43 mmol, 76%) of **6** as a colorless liquid: 90-MHz ^{1}H NMR δ 7.41 (4 H, s, Ar), 6.73 (1 H, dd, J = 10.7 Hz, =CH), 5.74, 5.24 (2 H, dd, J = 17.7, 10.7 Hz, CH_2=), 5.49 (1 H, s, CHO), 3.84–3.44 (4 H, m, OCH_2), 1.23 (6 H, t, J = 6.9 Hz, CH_3); 23-MHz ^{13}C NMR ($CDCl_3$) δ 15.2 (CH_3), 60.9 (CH_2), 101.3 (CHO), 113.9 (CH_2=), 126.0, 126.8 (Ar, C2 or C3), 136.6 (=CH), 137.6, 138.8 (Ar, C1 or C4).

(4-Vinylphenyl)dibutoxymethane (7). A solution of 4-vinylbenzaldehyde (6.60 g, 50 mmol), dry butanol (15.0 g, 20 mmol), *p*-toluenesulfonic acid (25 mg), and *tert*-butylcatechol (1 mg) in benzene (100 mL) was heated at reflux with azeotropic removal of water for 20 h.[8] The solution was washed with 10% $NaHCO_3$ and water and then dried over $MgSO_4$. Filtration and evaporation gave a pale yellow oil, which was purified by fractional distillation. A total of 6.4 g (25 mmol, 50%) of 7 was distilled at 108–112 °C (1 mmHg): 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.42 (4 H, s, Ar), 6.74 (1 H, dd, J = 10.8 Hz, =CH), 5.75, 5.25 (2 H, dd, J = 18.0, 10.8 Hz, CH_2=), 5.50 (1 H, s, CHO), 3.65–3.42 (4 H, m, OCH_2), 1.66–1.27 (8 H, m, CH_2CH_2), 0.9 (6 H, m, CH_3); 23-MHz ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 19.5 ($CH_2CH_2CH_2CH_3$), 32.0 ($CH_2CH_2CH_2CH_3$), 65.1 (OCH_2), 101.4 (CHO), 113.9 (CH_2=), 126.0, 126.9 (Ar, C2 or C3), 136.6 (=CH), 137.5, 138.8 (Ar, C1 or C4).

Polymerization Procedure. All polymerizations were carried out at −78 °C for 0.2–3 h with shaking under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with breakseals 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 methanol. 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: 90-MHz ^{1}H NMR ($CDCl_3$) δ 7.2–6.4 (4 H, m, Ar), 5.6 (1 H, s, CHO), 3.9 (4 H, m, (CH_2CH_2), 2.1–1.1 (3 H, m, CH_2CH).

Similarly, block copolymerization was carried out by sequential polymerizations of **3b** with styrene, styrene with **3b**, and **4** with styrene.

Deprotection of Poly(3b). Poly(**3b**) (0.420 g) was dissolved in 1,4-dioxane (5 mL) and cooled to 5 °C. HCl (2 N; 2 mL) was added dropwise to the solution, and the mixed solution was stirred at 5 °C for 3 h. The polymer was recovered by precipitation in water and purified by two reprecipitations from THF solution to hexane. The yield of polymer was quantitative (0.330 g, ~100%). The polymer was identified as poly(3-vinylbenzaldehyde) by its IR and ^{1}H NMR spectra: 90-MHz ^{1}H NMR ($CDCl_3$) δ 9.9 (1 H, s, CHO), 7.8–6.2 (4 H, m, Ar), 2.5–0.5 (3 H, m, CH_2CH); IR 1690 cm^{-1} (C=O).

Similarly, the deprotection reaction of poly(**4**) was carried out. The polymer gradually precipitated as the reaction proceeded. The polymer was recovered by precipitation in water. The THF-soluble part and THF-insoluble part were analyzed by ^{1}H NMR and IR spectroscopy and IR spectroscopy, respectively. The analyses indicated both parts to be only partly deprotected. Longer reaction time at 0 °C and/or the use of *p*-toluenesulfonic acid always gave small amounts of soluble polymers along with significant amounts of insoluble polymers, both of which were only partly deprotected.

Measurements. Infrared (IR) spectra were recorded on a Jasco IR-G spectrophotometer. ^{1}H NMR and ^{13}C 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 relative to $CDCl_3$ (δ 77.1) for ^{13}C NMR. Size exclusion chromatograms (SEC) for characterization of molecular weight distribution were obtained at 40 °C with a Toyo Soda HLC-802 instrument with ultraviolet or refractive index detection. 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

It is now well established that acyclic and cyclic acetals are able to promote the lithiation of an aromatic ring at the ortho position by proton–metal exchange to afford ortholithiated arenes with acetal groups.[11-16] Some synthetic examples of organolithium compounds containing acetal functionalitites have also been reported.[17-21] These demonstrations strongly suggest that the acetal functions are stable to the condition of anionic living polymerization where highly reactive carbanionic species are always present. Therefore, the anionic polymerizations of the acetal-protected styrene derivatives mentioned above are expected to proceed without difficulty.

Table I
Anionic Polymerization of 3b with Various Initiators in THF at −78 °C for 10–15 min[a]

3b, mol	initiator type	initiator 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]
3.89	cumyl K[e]	0.105	0.210	6.5	6.3	1.08
3.29	K-Nap[f]	0.145	0.428	8.7	7.9	1.18
4.08	K-Nap	0.0939	0.313	16	14	1.14
4.56	cumyl K	0.0264	0.0607	31	29	1.13
7.44	cumyl K	0.0131	0.0301	100	96	1.21
3.97	Li-Nap[g]	0.131	0.330	11	12	1.29
5.17	BuLi[h]	0.0330	0.383	29	44	1.60
7.50	BuLi	0.0250	0.145	58	120	2.70

[a] Yields of polymers with 95–100%. [b] α-Methylstyrene. [c] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution. [d] $\bar{M}_w/\bar{M}_n$ was calculated from the SEC curve, using standard polystyrenes for calibration. [e] Cumylpotassium. [f] Potassium naphthalenide. [g] Lithium naphthalenide. [h] Butyllithium.

Anionic Polymerization of 3b. The anionic polymerization of **3b** (meta isomer) was carried out in THF at −78 °C with mono- or difunctional oligo(α-methylstyryl)lithium and -potassium. The reaction mixtures always exhibited a reddish orange color for Li^+ as counterion and a dark red color for K^+, indicating the generation of polystyryl anions derived from **3b**. The color apparently remained unchanged at −78 °C after 24 h but disappeared immediately when a few drops of methanol was added. The polymer was then precipitated by pouring the reaction mixture into a large amount of methanol, giving a near-quantitative yield in each case. The polymer was purified by repeated precipitation in THF–methanol.

Direct evidence for the expected structure of poly[2-(3-vinylphenyl)-1,3-dioxolane] by vinyl polymerization came from the IR and ^{1}H NMR spectra of the resulting polymer. The characteristic signals at 5.6 and 3.8 ppm for the 1,3-dioxolane ring were clearly observed at reasonable integral ratios to the other signals. Furthermore, both signal and absorption corresponding to the formyl group were not detected at all. Accordingly, the acetal functions stayed intact during the course of the polymerization and the reprecipitation steps.

The molecular weights and the distribution parameters, $\bar{M}_w/\bar{M}_n$, for this series of polymers are listed in Table I. As can be seen in the polymer samples obtained by the use of oligo(α-methylstyryl)potassium and -dipotassium as initiators, there is a fair agreement between the predicted $\bar{M}_n$s from [M]/[I] and the observed values by VPO. The SEC analyses reveal unimodal peaks with narrow distributions ($\bar{M}_w/\bar{M}_n < 1.2$) for all polymer samples. The results obtained by VPO and SEC clearly indicate that **3b** undergoes anionic living polymerization where chain transfer and termination reactions are not detectable. Furthermore, rapid initiation is consistent with the fact that the polymers have narrow molecular weight distributions. It is therefore obvious that the 1,3-dioxolane ring successfully protects the formyl group of 3-vinylbenzaldehyde during the course of the anionic living polymerization.

On the other hand, the results with the use of oligo(α-methylstyryl)lithium and -dilithium as initiators are not very satisfactory from the viewpoint of living polymerization. In the polymer samples obtained, deviation between the measured and calculated $\bar{M}_n$ values was observed, the former values always being higher than the latter ones. The molecular weight distributions were always somewhat broad. Both the low and high molecular weight parts in addition to the main peaks were clearly observed in the SEC peaks of the polymers having $\bar{M}_n > 10^5$. This may be due—at least in part—to the probability of undesirable side reactions occurring during the polymerization of **3b** with these initiators. The metalation at the acetal proton may be a candidate for the side reaction, since it is often observed in the reactions of acetals of benzaldehyde and organolithium reagents.[22] Thus, the choice of the initiator is important and the organopotassium compounds are preferable as initiators, especially for the synthesis of well-defined poly[2-(3-vinylphenyl)-1,3-dioxolane] with respect to molecular weight and molecular weight distribution.

Removal of the Acetal Protecting Group in Poly[2-(3-vinylphenyl)-1,3-dioxolane]. Complete deprotection is very important in the synthesis of polymers with a protecting group, since separation of the protected and deprotected forms in the same polymer chain is, in principle, impossible. The 1,3-dioxolane ring in the polymer was readily cleaved to generate the aldehyde function by treating the poly[2-(3-vinylphenyl)-1,3-dioxolane] with 0.5 N HCl in 1,4-dioxane–water (3/1, v/v) at 5 °C for 3 h. The deprotected polymer was completely recovered by precipitation in water.

The IR spectrum of the resulting polymer exhibited a strong band at 1690 cm^{-1} characteristic for the aldehyde function and was virtually identical with that of poly(3-vinylbenzaldehyde) obtained by conventional radical polymerization. The ^{1}H NMR spectrum showed the signals expected for poly(3-vinylbenzaldehyde). The signal for the aldehyde proton was present at 9.9 ppm, whereas no trace of the signals corresponding to the 1,3-dioxolane ring at 5.6 and 3.8 ppm could be detected. Thus, the spectroscopic studies reveal within their analytical limits that the complete removal of the protecting group from the polymer of **3b** is achieved.

The poly(3-vinylbenzaldehyde) obtained is a white solid and has a solubility behavior very similar to that of poly(4-vinylbenzaldehyde) reported in the previous paper.[3] It is soluble in THF, 1,4-dioxane, methyl ethyl ketone, chloroform, dichloromethane, and *N*,*N*-dimethylformamide but is insoluble in hexane, benzene, toluene, carbon tetrachloride, diethyl ether, ethyl acetate, acetone, carbon disulfide, butanol, ethanol, methanol, and water.

The SEC profile of the resulting poly(3-vinylbenzaldehyde) shows that the peak is unimodal and elutes within a reasonable molecular weight region. The shape of the peak is nearly identical with that of the original polymer, suggesting that neither main-chain degradation nor branching occurs during the deprotection step. Thus, we are successful in synthesizing soluble, linear poly(3-vinylbenzaldehydes) of predicted molecular weights and of narrow molecular weight distributions.

Synthesis of Block Copolymers Containing Poly(3-vinylbenzaldehyde) Sequences. The synthesis of the block copolymer was successfully demonstrated by the sequential polymerization of **3b** (monomer A) and styrene (monomer B) with oligo(α-methylstyryl)dipotassium in THF at −78 °C. The yield of polymer was quantitative. The results summarized in Table II show that the resulting polymer possesses an $\bar{M}_n$ in close accord with the predicted value. The composition of each block determined by the ^{1}H NMR spectrum was found to be nearly equal to that calculated from both monomers used in the polymerization. The SEC analysis showed that the peak of the starting polymer of **3b** block shifted toward the higher molecular weight side after addition of styrene. Furthermore, the resulting polymer possesses a narrow molecular weight distribution. All of the evidence from these results clearly indicates that the living polymer of **3b** initiates the polymerization of styrene to afford a well-defined BAB-type triblock copolymer.

Table II
Block Copolymerizations of 3b and Styrene in THF at −78 °C with Oligo(α-methylstyryl)dipotassium[a]

type of block copolymer	A monomer	B monomer	$10^{-3}\bar{M}_n$(calcd)	$10^{-3}\bar{M}_n$(obsd)[b]
BAB	**3b**	styrene	32	32[c]
ABA	**3b**	styrene	31	30[d]

[a] Yields of polymers were 98–100%. [b] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution. [c] $\bar{M}_w/\bar{M}_n = 1.11$. [d] $\bar{M}_w/\bar{M}_n = 1.12$.

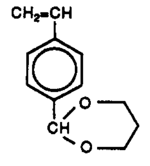
Similarly, an ABA-type triblock copolymer could be prepared by the reverse addition of monomers with oligo(α-methylstyryl)dipotassium. The analyses of VPO, SEC, and ^{1}H NMR measurements reveal formation of the expected block copolymer as shown in Table II.

Deprotection of the poly(**3b**) sequences in both the ABA and BAB block copolymers was successfully achieved without difficulty in a manner similar to that described above. Thus, new types of block copolymers having poly(3-vinylbenzaldehyde) sequences with controlled $\bar{M}_n$s are prepared by means of the anionic living polymerizations of **3b** and styrene.

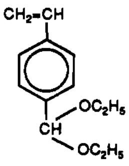
Anionic Polymerizations of 3a and 3c. The polymerization of the meta isomer **3b** is a typical anionic "living system". On the contrary, the anionic polymerizations of the ortho and para isomers, **3a** and **3c**, exhibit unusual features, giving polymers with very broad molecular weight distributions or insoluble products in only low yields. Well-defined polymer samples from both **3a** and **3c** could not be obtained at all. This is the most puzzling feature observed in this work and will be discussed in this section.

As mentioned before, in the preliminary experiment we failed to polymerize the para isomeric monomer, **3c**, with either sodium naphthalenide or oligo(α-methylstyryl)disodium in THF at −78 °C. Since the result was unexpected considering the stability of the acetal function toward carbanions, more detailed experiments on the polymerization of **3c** were carried out in THF at −78 °C with the following initiators: lithium, sodium, and potassium naphthalenides, butyllithium, and oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium. In each of the cases, the characteristic red coloration was observed at first on mixing of the initiator and monomer solutions. The color did, however, disappear within a few minutes. Small amounts of insoluble products were obtained along with 80–90% recovery of the starting **3c** in all cases. No attempt was made to identify the structures of the insoluble products.

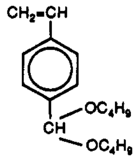
Similarly, no appreciable polymerization of the 1,3-dioxane derivative **5** of 4-vinylbenzaldehyde occurred with lithium naphthalenide, potassium naphthalenide, or oligo(α-methylstyryl)dipotassium. The diethyl acetal (**6**) and dibutyl acetal (**7**) derivatives appeared to undergo anionic



(5)



(6)



(7)

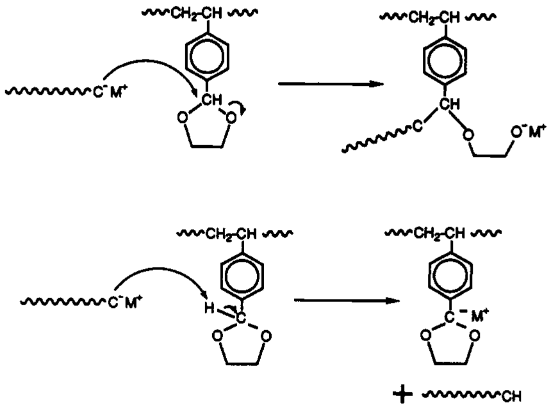
polymerizations with oligo(α-methylstyryl)dipotassium. The reaction mixtures were always clear red solutions for at least 10 min but became jelly-like masses which included the whole of the liquid present after 0.5 h. Insoluble polymers were finally obtained in 90% yield from **6** and 53% yield from **7**. Their IR spectra showed the disappearance of the bands corresponding to the vinyl groups and were indicative of the polymer structures obtained by vinyl polymerizations of **6** and **7**. Since the products are insoluble in the usual organic solvents, they may be cross-linked polymers of **6** and **7**.

The addition of **3c** to the living polymer of either styrene or α-methylstyrene always resulted in the immediate formation of insoluble gelatinous materials in THF at −78 °C. Their IR spectra indicated that they mostly consisted of polystyrene and poly(α-methylstyrene). These polymers either are cross-linked or become insoluble in the organic solvents. Since most of the starting monomer was recovered in both cases, the side reaction proposed below might occur at a very early stage of these polymerizations.

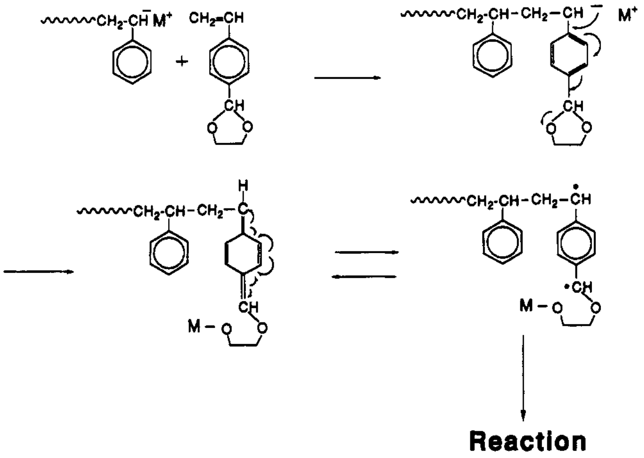
Similarly, difficulty was encountered in the anionic polymerization of the ortho isomeric monomer, **3a**. The polymerization was carried out under conditions identical with those employed for **3b** and **3c**. The initiators used were lithium napthalenide, potassium naphthalenide, and oligo(α-methylstyryl)dilithium and -dipotassium. The reaction mixtures were always red, which still remained at −78 °C after 3 h. Soluble polymers were obtained, but the yields were surprisingly low (~10%) even after a longer reaction time of 3 h. **3a** was recovered (70–90%) in all cases. The SEC profiles of the resulting polymers showed that they had molecular weights of 10^3–10^4 and multimodal peaks with very broad molecular weight distributions. The ^{1}H NMR spectra were indicative of the structure of poly(**3a**). The resulting poly(**3a**)s obtained may possibly be highly branched polymers. Obviously, undesirable side reactions occur to a significant extent during the course of the polymerization of **3a**.

Thus, all attempts failed to synthesize well-defined polymers by the anionic polymerizations of **3a** and **3c** and the related monomers **5**, **6**, and **7**. The polymerization of the ortho isomer **3a** always gave soluble polymers of very broad molecular weight distributions in surprisingly low yields. Even soluble polymers were not obtained at all in the anionic polymerizations of the para-substituted isomers **3c**, **5**, **6**, and **7**.

For the cause of the failure of the anionic living polymerizations of these monomers, we first consider the reactions of the acetal functionality with the carbanions of the initiator and the active end of the polymer chain. Possible candidates are the reductive cleavage of the acetal function[19,23] and the metalation reaction at the 2-position of the 1,3-dioxolane ring.[22] However, the possibility of such reactions can be ruled out from the observation that both polystyryllithium and -potassium are stable in the presence of a large excess (20–30 equiv relative to the carbanions) of monomer model compounds such as 2-phenyl-1,3-dioxolane and the diethyl acetal of benzaldehyde. No loss of living ends was observed at −78 °C even after 24 h. The successful demonstration of the anionic living polymerization of **3b** also suggests that the above side reactions do not take place in the anionic polymerizations of **3a** and **3c**. Accordingly, the complication in the polymerizations of **3a** and **3c** is not related to the reactions of the acetal function with carbanions but appears to be due to the inherent structures of the monomers.



We therefore propose an alternative and more likely mechanism to explain the above experimental observations. The proposed mechanism is that the carbanion at the polymer chain end may induce 1,6-elimination (or 1,4-elimination for the ortho isomer) of the acetal to generate the very reactive *p*-xylylene (or *o*-xylylene) intermediate, which reacts readily by radical combination to form a cross-linked polymer network, as shown below for the case of the para isomer:



Some suggestive observations and mechanisms for this have been already reported by Rickborn and co-workers in the reactions of the dimethyl acetal of 2-methylbenzaldehyde and related compounds with nonnucleophilic strong bases.[24,25] They proposed base-induced 1,4-elimination of the acetals to generate the very reactive *o*-xylene intermediate. The key point of their mechanism is that it is effective for the ortho and probably para isomers but not the meta isomer. This fits well with our results for the anionic polymerizations of **3a**, **3b**, and **3c**.

In the anionic polymerization of **3c**, the elimination reaction should compete with the polymerization. The elimination and the subsequent reactions of the xylylene intermediate seem to be fast and are completed within a few minutes, in view of the observations that the characteristic red color in the reaction mixture disappears rapidly and that insoluble polymers are formed immediately on mixing of **3c** and the living polymers of styrene and α-methylstyrene.

In the polymerization of **3a**, both the polymerization and the elimination reactions may be slow, or there may be an equilibrium between both reactions, probably due to the steric hindrance from the bulky 1,3-dioxolane ring at the ortho position, resulting in the formation of soluble poly[2-(3-vinylphenyl)-1,3-dioxolanes] of very broad molecular weight distributions which are estimated to be highly branched. Although the proposed mechanism is tentative and there is no direct evidence at the present

Table III
Anionic Polymerization of 4 with Oligo(α-methylstyryl)dipotassium in THF at −78 °C for 10 min[a]

4, mmol	initiator, 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]
2.35	0.142	0.334	6.8	6.9	1.12
3.29	0.158	0.250	10	10	1.10
3.14	0.0998	0.301	13	15	1.12
3.08	0.0647	0.175	19	20	1.09

[a] Yields of polymers were 94–97%. [b] α-Methylstyrene. [c] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution. [d] $\bar{M}_w/\bar{M}_n$ was calculated from the SEC curve, using standard polystyrenes for calibration.

time, this can satisfactorily explain the experimental results of the polymerizations of **3a**, **3b**, and **3c**.

Anionic Polymerization of 4. In this section we describe the anionic polymerization of the protected monomer 4, where the aliphatic aldehyde is protected in the form of a 1,3-dioxolane, similar to case for **3a**, **3b**, and **3c**. The anionic polymerization was carried out in THF at −78 °C for 10 min with oligo(α-methylstyryl)dipotassium. The reaction mixture always exhibited the characteristic red color, and there was no apparent change at −78 °C for 24 h. The polymer solution was terminated with a few drops of methanol and was then poured into a large amount of methanol to precipitate the polymer. The yield of polymer was quantitative in each case based on the polymer weights. Cleavage of the 1,3-dioxolane ring could not be observed by the ^{1}H NMR analysis of the resulting polymer.

As can be seen in Table III, the agreement between the values of $\bar{M}_n$ observed by VPO and those calculated from [M]/[I] indicates that a good molecular weight control is possible in the polymerization. The SEC profiles showed that all of the polymer samples possessed single peaks without shoulders and narrow molecular weight distributions, the $\bar{M}_n/\bar{M}_n$ values being around 1.1. These results reflect the living nature of the anionic polymerization of 4.

Additional direct evidence for the presence of living poly(4) is provided by the successful formation of block copolymer by addition of styrene to the polymeric anion prepared from 4 with oligo(α-methylstyryl)dipotassium. The analyses of the resulting block copolymer by ^{1}H NMR, VPO, and SEC show that the polymer possesses the predicted molecular weight ($\bar{M}_n$(calcd) = 12 000 vs $\bar{M}_n$(obsd) = 10 000), composition, and narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.08). These data clearly demonstrate that the aliphatic aldehydes can also be completely protected during the anionic living polymerizations by converting to 1,3-dioxolane rings. Obviously, the presence of a substituted group at the para position is essentially no problem in the anionic polymerizations. The success of the anionic living polymerization of 4 also strongly supports the validity of the proposed mechanism to explain the unusual features observed in the polymerizations of **3a** and **3c**, since the occurrence of the elimination reaction according to the mechanism is not possible in the polymerization of 4.

Unfortunately, the deprotection to the aliphatic aldehyde from the resulting poly(4) was difficult under the acidic conditions. The treatment of the polymer with 0.5 N HCl or a small amount of *p*-toluenesulfonic acid always led to the formation of insoluble polymers, probably due to the acid-catalyzed oligomerization and/or condensation of aliphatic aldehydes in the polymers resulting in the cross-linking between the polymer chains. More careful treatment will be required in this deprotection step.

In summary, we tried to polymerize the acetal-protected styrene derivatives **3a**, **3b**, **3c**, and **4–7** with anionic initiators. Among them, the anionic polymerizations of **3b** (meta isomer) and **4** are norml and give living polymers, producing well-defined polymers with respect to chain length. The results indicate that the acetals are essentially effective for protection of both aromatic and aliphatic aldehyde functions under the anionic living polymerization. On the other hand, complications were observed in the polymerizations of the ortho and para isomers, **3a**, **3c**, and **5–7**. Thus, it was found that the anionic polymerization behavior was significantly influenced by the position of acetal substitution in the aromatic ring in the monomer. The use of monomers with direct attachment of acetal groups on the aromatic ring at the ortho and/or para positions always causes a problem in anionic polymerizations. The base-induced elimination of acetal to regenerate the *p*(or *o*)-xylylene intermediate was proposed as a mechanism to explain the results of polymerizations of both the ortho and the para isomeric monomers. To our knowledge, this is the first clear example that shows the positional effect of the substituent in the anionic polymerization of styrene derivatives. Attention should be paid to such an effect in the anionic polymerization.

References and Notes

(1) For reviews of this series, see: Nakahama, S.; Hirao, A. *J. Synth. Org. Chem. Jpn.* **1986**, *44*, 137. Nakahama, S.; Hirao, A. *Prog. Polym. Sci.* **1990**, *15*, 299. For recent papers of this series, see for example: Suzuki, K.; Yamaguchi, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2607. Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2895.

(2) Hirao, A.; Ishino, Y.; Nakahama, S. *Makromol. Chem.* **1986**, *187*, 141.

(3) Hirao, A.; Nakahama, S. *Macromolecules* **1987**, *20*, 2968.

(4) Green, T. W. *Protective Groups in Organic Synthesis*: Wiley-Interscience: New York, Chichester, Brisbane, Toronto, 1981; pp 116.

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

(6) Morton, M.; Rembaum, A. A.; Hall, J. L. *J. Polym. Sci., Part A* **1963**, *1*, 461.

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

(8) Smith, S. W.; Newman, M. S. *J. Am. Chem. Soc.* **1968**, *90*, 1249, 1253.

(9) Olah, G. A.; Ohannesian, L.; Arranaghi, M. *J. Org. Chem.* **1984**, *49*, 3856.

(10) DeGraw, J. I.; Goodman, L.; Baker, B. R. *J. Org. Chem.* **1961**, *26*, 1156.

(11) Christensen, H. *Synth. Commun.* **1975**, *5*, 65.

(12) Plaumann, H. P.; Keay, B. A.; Rodrigo, R. *Tetrahedron Lett.* **1979**, 4921.

(13) Townsend, C. A.; Blood, L. M. *Tetrahedron Lett.* **1981**, 3923.

(14) Winkel, M. R.; Ronald, R. C. *J. Org. Chem.* **1982**, *47*, 2101.

(15) Napolitano, E.; Giannone, E.; Fiaschi, R.; Marsili, A. *J. Org. Chem.* **1983**, *48*, 3653.

(16) Narasimhan, N. S.; Ranade, A. C.; Deshpande, H. R.; Gokhale, U. B.; Jayalakshmi, G. *Synth. Commun.* **1984**, *14*, 373.

(17) Schulz, D. N.; Halasa, A. F.; Oberster, A. E. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 153.

(18) Chenard, B. L.; Manning, M. J.; Raynolds, P. W.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 378.

(19) Swenton, J. S.; Anderson, D. K.; Jackson, D. K.; Narasimhan, L. J. *J. Org. Chem.* **1981**, *46*, 4825.

(20) Spangler, L. A.; Swenton, J. S. *J. Org. Chem.* **1984**, *49*, 1800.

(21) Hartman, G. D.; Phillips, B. T.; Halczenko, W. *J. Org. Chem.* **1985**, *50*, 2423, 2427.

(22) Meyers, A. I.; Campbell, A. L. *Tetrahedron Lett.* **1979**, 4155.

(23) Ho, T. L. *Synth. Commun.* **1983**, *13*, 769.

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

(25) Moss, R. J.; White, R. O.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 5132.