Protection and Polymerization of Functional Monomers. 24. Anionic Living Polymerizations of 5-Vinyl- and 4-Vinyl-1,3-benzodioxoles

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ABSTRACT: Anionic polymerizations of 5-vinyl-1,3-benzodioxole (**1**) and 4-vinyl-1,3-benzodioxole (**2**) were carried out in tetrahydrofuran at −78 °C with oligo(α-methylstyryl)dilithium and -dipotassium. The vinyl polymerizations of **1** and **2** proceeded quantitatively within 30 min. The resulting polymers had predicted molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.1$), indicating the living character of the polymerization systems. These living polymers were however found not to be completely stable either for a long time (24 h) or at an elevated temperature (−30 °C). Well-defined block copolymers, poly(**1**-*b*-styrene-*b*-**1**), poly(styrene-*b*-**1**-*b*-styrene), and poly(styrene-*b*-**2**), were successfully synthesized by the sequential polymerizations. The methylenedioxy linkage of the acetal moiety of poly(**1**) was completely cleaved with boron tribromide–dimethyl sulfide complex in 1,2-dichloroethane to give the unstable poly(4-vinylcatechol).

Introduction

Development of a system suitable for the living anionic polymerization of functional monomers has attracted considerable attention of a number of polymer chemists, since it enables one to produce new (co)polymers having well-defined chain structures such as controlled molecular weights, narrow molecular weight distributions, regulated block lengths, and tailored compositions. However, functional monomers capable of anionic living polymerization have been extremely limited because the reactive functional groups of the monomers and the polymers are easily attacked by the anionic initiators and the propagating carbanions during the course of the polymerization.

In order to overcome these problems, we have introduced a concept of protecting groups into polymer synthesis by means of anionic living polymerizations.[1] The method involves the anionic living polymerization of the protected functional monomers and the deblocking of the protecting groups to regenerate the original functional groups. This protecting method has been widely proved as a strong tool for the syntheses of a series of novel functional polymers with controlled molecular architecture. In fact, a series of homopolymers and block copolymers of styrenes substituted with OH,[2] SH,[3] NH_2,[4] CHO,[5] $COCH_3$,[6] COOH,[7] and C≡CH[8] groups could be successfully synthesized through this method.

In a part of our studies on this method, we have paid attention to the synthesis of well-controlled poly(vinylcatechol)s by way of the anionic living polymerization of the protected vinylcatechols. The reason for the choice of catechol as a new functional moiety is that catechols are known to show interesting reactivities in many important reactions such as oxidation and reduction reactions involving oxyl radicals[9] and electrophilic substitution. Their abilities of bidentate chelation to the metal ions as well as the acidities of 1,2-disubstituted phenolic OH groups are also interesting properties of catechols.[10]

The protected monomer candidates are 5-vinyl-1,3-benzodioxole (**1**) and 4-vinyl-1,3-benzodioxole (**2**) (Chart 1). Their catecholic two adjacent OH groups are simultaneously protected by the methylenedioxy acetal bondings. These monomers were previously prepared by Daly and his co-workers.[11] They also attempted the anionic polymerizations of **1** and **2** under conventional conditions using sodium naphthalenide and *n*-butyllithium. However, only low molecular weight polymers were obtained in low yields under the conditions employed. These results are questionable for us, since it has been reported by numerous investigators that dioxole and the related acetal functions are considerably stable under conditions using strong bases and nucleophiles and the lithiation reactions.[12] Moreover, we have recently demonstrated that the anionic polymerization of styrenes containing acetal linkages affords the stable living polymers (Chart 2).[5c] These fruitful reports about the stability of the acetal moiety encouraged us to reinvestigate the anionic polymerization of **1** and **2**, acetal-protected dihydroxy-substituted styrenes, in more detail to examine the possibility of their living polymerizations thoroughly under various conditions.

Results and Discussion

As mentioned in the Introduction, Daly and his coworkers attempted the anionic polymerization of **1** and **2**.[11] Under the conditions with *n*-butyllithium in benzene at room temperature, for example, the yields of the resulting poly(**1**) and poly(**2**) were disappointingly low and far from quantitative (23 and 8%, respectively). These results suggest that the nucleophilic attack of the propagating carbanion toward the acetal linkages might take place during the polymerization of **1** and **2**, although the authors have mentioned the insufficient purification of the monomers used in the polymerization.[11b]

In order to examine the possibility of living polymerization of **1** and **2**, we have here employed various anionic initiators such as *n*- and *sec*-butyllithiums,

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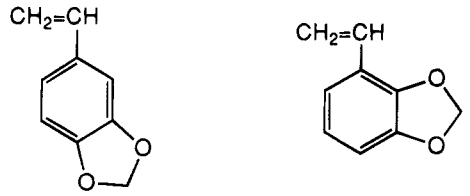
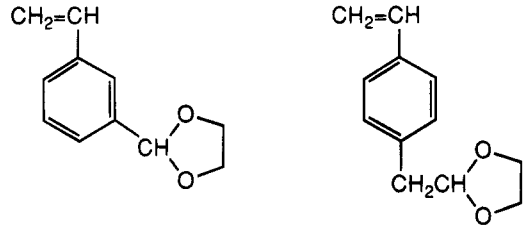
Chart 1



1 2

Chart 2



lithium, sodium, potassium naphthalenides, and living oligomers of α-methylstyrene associated with Li^+, Na^+, and K^+. The anionic polymerizations were performed in THF at low temperature (mainly at −78 °C) under high-vacuum conditions (10^{-6} mmHg). We carefully purified **1** and **2** by fractional distillations over calcium hydride at first and then over phenylmagnesium chloride on a vacuum line.

Anionic Polymerization of 1 and 2. The anionic polymerization of **1** was first carried out in THF at −78 °C with either *n*-butyllithium or *sec*-butyllithium. The color of the polymerization systems immediately changed to a characteristic red on the addition of **1** in THF to the butyllithiums. The reaction mixtures maintained the red coloration during the course of polymerization until a small amount of methanol was added to terminate the reaction. This strongly indicates that the polystyryl anion formed in both polymerization systems. The polymers were always quantitatively obtained after pouring the polymerization solution into a large excess of methanol to precipitate. The polymerizations of **1** with butyllithiums were always complete within 0.5−1 h at −78 °C in THF. These quantitative yields of the resulting polymers are in marked contrast to the results reported previously by Daly and his co-workers.[11] Table 1 shows the polymerization results of **1** with various anionic initiators including the butyllithiums at −78 °C in THF. The molecular weights of the polymers were measured by vapor pressure osmometry (VPO) in benzene. The polydispersity index (M_w/M_n), which shows the molecular weight distribution of poly(**1**), was estimated from the SEC calibration by using standard polystyrenes in THF. Although the poly(**1**)s produced with butyllithiums possessed narrow molecular weight distributions of unimodal SEC curves, the observed number-average molecular weights of the polymers greatly deviated from the predicted values based on the molar ratios between monomer and employed butyllithiums. A similar result was obtained in the polymerization initiated with difunctional lithium maphthalenide. These experimental results suggest that some side reactions occur at the initial stage of the polymerization initiated with butyllithiums and lithium naphthalenide, despite the quantitative conversion of monomer and narrow molecular weight distributions of the polymers.

On the other hand, the polymerizations initiated with living oligomers of α-methylstyrenes containing lithium

Table 1. Anionic Polymerization of 1 and 2 in THF at −78 °C for 0.5−1 h[a]

run	monomer, mmol	initiator, mmol	α-MeSt,[b] mmol	$10^{-3}M_n$ calcd[c]	$10^{-3}M_n$ VPO[d]	M_w/M_n[e]
1	**1**, 4.92	*n*-BuLi, 0.0710		10	19	1.14
2	**1**, 4.63	*sec*-BuLi, 0.0524		13	22	1.02
3	**1**, 3.79	Li-Naph,[f] 0.103		11	19	1.04
4	**1**, 4.20	*sec*-BuLi, 0.0679	0.282	10	12	1.02
5	**1**, 3.69	Li-Naph, 0.110	0.316	11	11	1.05
6	**1**, 5.80	Li-Naph, 0.0924	0.262	19	20	1.07
7	**1**, 7.47	Li-Naph, 0.0736	0.301	31	33	1.05
8[g]	**1**, 3.61	Li-Naph, 0.0685	0.293	17	19	1.13
9[h]	**1**, 3.37	Li-Naph, 0.0768	0.308	14	16	1.30
10	**1**, 4.11	Na-Naph,[i] 0.111		11	35	1.14
11	**1**, 5.32	Na-Naph, 0.126	0.365	13	18	1.69
12	**1**, 3.74	K-Naph,[j] 0.108		10	41	1.11
13	**1**, 3.53	K-Naph, 0.0958	0.269	12	16	1.19
14	**2**, 2.79	Li-Naph, 0.0782	0.297	11	11	1.05
15	**2**, 3.16	*sec*-BuLi, 0.0161	0.313	31	37	1.02
16	**2**, 2.98	K-Naph, 0.0940	0.314	10	10	1.05
17	**2**, 3.40	K-Naph, 0.0531	0.268	20	20	1.05

[a] Yields of polymers were almost quantitative in each case. [b] α-Methylstyrene. [c] M_n(calcd) = ([monomer] × (MW of monomer) × *f*/[initiator]) + MW of initiator; *f* = 1 or 2, corresponding to the functionality of the initiators. [d] M_n(VPO) was obtained by VPO in benzene. [e] M_w/M_n was estimated from SEC calibration by using standard polystyrenes in THF solution. [f] Lithium naphthalenide. [g] For 24 h. [h] At −30 °C. [i] Sodium naphthalenide. [j] Potassium naphthalenide.

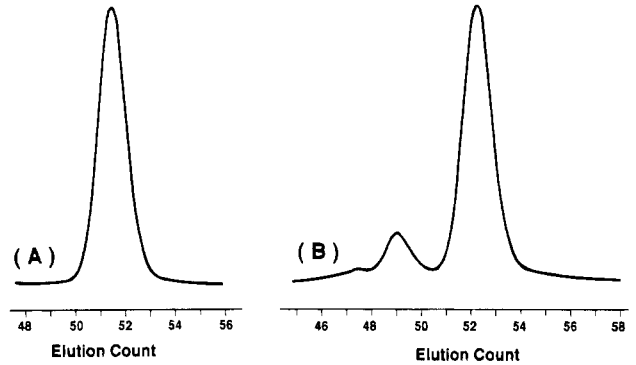
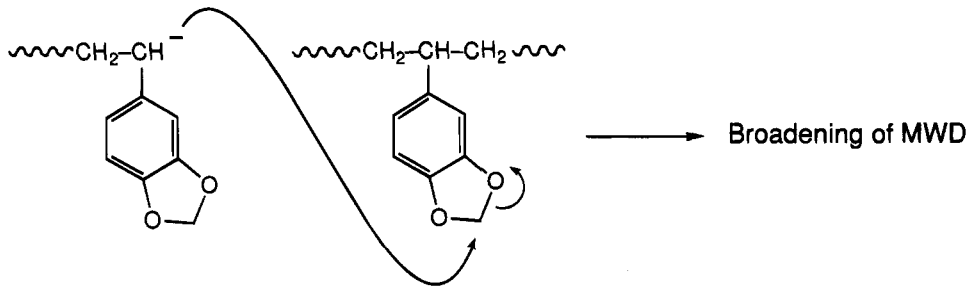


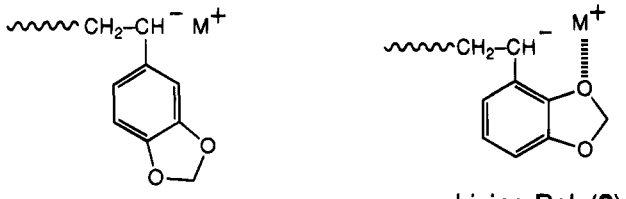
Figure 1. SEC curves of poly(**1**)s obtained at −78 °C for 1 h (A), M_n(obsd) = 33 000, M_w/M_n = 1.05; and at −78 °C for 24 h (B), M_n(obsd) = 19 000, M_w/M_n = 1.13.

countercation yielded quantitatively the poly(**1**)s having the predicted molecular weights in addition to the narrow molecular weight distributions (Figure 1A). Fine control of molecular weights of the polymers in the M_n range 10 000−30 000 was attained by using the oligo(α-methylstyryl)lithium and the corresponding difunctional dilithium salt. In addition, the propagating chain end of poly(**1**) was shown to be stable at −78 °C at least for 0.5 h as described later in the section of block copolymerization. The results obtained here clearly show that a stable living polymer forms in the anionic polymerization of **1** with oligo(α-methylstyryl) anions at −78 °C in THF. The less basic and/or less nucleophilic benzylic carbanion of oligo(α-methylstyryl)lithium seems to suppress the undesirable side reactions at the initiation step of **1**. However, allowing the reaction mixture to stand for 24 h at −78 °C (Table 1, run 8), the SEC trace of the polymer became slightly broader and had a small shoulder at the higher molecular weight side in addition to the sharp main peak (Figure 1B). Raising the polymerization temperature to −30 °C also gave a polymer of broad molecular weight distribution (M_w/M_n = 1.30). These observations suggest that the propagating carbanion of the poly(**1**) is not stable at −78

Scheme 1



Scheme 2



°C for 24 h as well as at −30 °C. These side reactions are negligible for a short period at least for 0.5−1 h at −78 °C as previously evidenced in runs 4−7. From the fact of the broadening of the molecular weight distribution, we can speculate that the most probable side reaction might be intra- and intermolecular nucleophilic attacks of the propagating carbanion on the O−C−O bond of acetal linkage in the poly(**1**) as shown in Scheme 1.

We tried to polymerize **1** with sodium naphthalenide, potassium naphthalenide, and oligo(α-methylstyryl)-disodium and -dipotassium under similar conditions. Unfortunately, the resulting poly(**1**)s had either higher molecular weights than those of the predicted values or broad molecular weight distributions. Some side reactions such as partial deactivation of the initiators and termination of the propagating species may occur at the initial stage of the polymerization. Thus, it is realized that the suitable selection of the polymerization temperature and the employed initiators is necessary for the precise control of the molecular weight and molecular weight distribution of the resulting poly(**1**) in the anionic living polymerization of **1**.

Next, the anionic polymerization of **2**, the 4-vinyl regioisomer, was investigated under similar conditions to **1**. The polymerization of **2** also proceeded quantitatively within 0.5 h and poly(**2**) was obtained in a quantitative yield, as can be also seen in Table 1. By contrast to the cases of **1**, the polymers having narrow molecular weight distributions and the predicted M_n values were always obtained, even when oligo(α-methylstyryl)dipotassium was employed as an initiator. This may derive from the different stability of the propagating species between poly(**1**) and poly(**2**). As illustrated in Scheme 2, in the polymerization of **2**, the plausible intramolecular coordination of the *ortho*-substituted ether oxygen atom to the terminal carbanion might lead to the stabilization of the terminal propagating carbanions to circumvent the side reactions, which were slightly observed in the polymerization of **1**.

In summary, we have successfully accomplished the anionic living polymerizations of two isomers of benzodioxole, **1** and **2**, in contrast to results previously reported.[11] The quantitative and well-defined polymer syntheses are thus successfully realized, although both the polymerization temperature and time and the choice of the initiator are actually found to be critical factors. The polymerization behaviors of **1** and **2** are somewhat different from each other, and the polymerization system of **2** seems to be more stable than that of **1** under the anionic conditions employed here. The positions of the substituents probably affect the polymerization behaviors of vinylbenzodioxoles by changing the stability of the active chain ends.

Block Copolymerization of 1 and 2 with Styrene and α-Methylstyrene. One of the most attractive features of living polymerization is the capability of the synthesis of the block copolymer having a known architecture. The attainment of the living polymerization of **1** and **2** encouraged us to synthesize novel block copolymers containing poly(**1**) and poly(**2**) segments.

The sequential polymerization of **1** and styrene was carried out with oligo(α-methylstyryl)dilithium in THF at −78 °C in order to synthesize a triblock poly(styrene-*b*-**1**-*b*-styrene). After the polymerization of **1** for 0.5 h, the propagating carbanion of poly(**1**) could initiate the second-stage polymerization of styrene to afford the polymer in quantitative yield. The composition of each polymer segment in the resulting polymer was determined by the ^{1}H NMR spectrum and was nearly equal to that of the feed ratio of **1** and styrene. Furthermore, the SEC analysis of the polymer showed that the peak of the starting homopoly(**1**) shifted to the higher molecular weight side after the addition of styrene as the second monomer. Obviously, as shown in Table 2 (run 18), the resulting polymer possesses a controlled molecular weight based on the molar ratio of both comonomers and the initiator and a narrow molecular weight distribution. We can conclude from the results obtained here that the living poly(**1**) quantitatively initiates the further polymerization of styrene to give a well-defined BAB triblock copolymer.

Similarly, a poly(**1**-*b*-styrene-*b*-**1**) of predicted molecular structure could be synthesized with the difunctional initiator by the sequential addition of both monomers (run 19). Thus, the "reversible" sequential copolymerization is possible between **1** and styrene to produce the tailor-made block copolymers of reversed sequence. This also indicates that reactivity of **1** under anionic conditions is nearly equal to that of styrene.

Other new block copolymers of **1** and α-methylstyrene and **2** and styrene were successfully prepared by means of the sequential addition of different monomers.

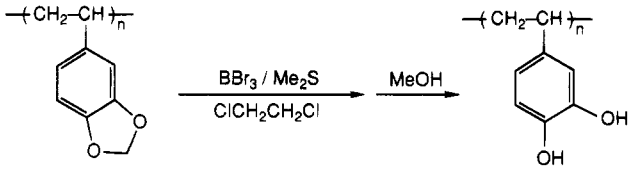
Deprotection of Poly(1). The deprotection of poly(**1**) thus obtained was carried out according to the modified procedure by Daly and his co-workers.[11] We here employed boron tribromide−dimethyl sulfide complex in a mixed solvent of 1,2-dichloroethane and methylene dichloride in order to liberate the catechol moiety under nitrogen at reflux temperature for 4.5 h (Scheme 3).[13] The polymer was observed to gradually

Table 2. Block Copolymerization of 1 and 2 with Styrene and α-Methylstyrene at −78 °C in THF[a]

run	block sequence	A monomer	B monomer	block copolymer (homopolymer[b]) $10^{-3}M_n$ calcd[c]	$10^{-3}M_n$ obsd[d]	M_w/M_n[e]
18	B–A–B	**1**	styrene	24 (11)	24 (11)	1.06 (1.06)
19	A–B–A	**1**	styrene	19 (8.8)	18 (8.3)	1.07 (1.19)
20	B–A	**1**	α-methylstyrene	20 (8.5)	18 (8.3)	1.07 (1.06)
21	B–A	**2**	styrene	10 (4.5)	12 (6.1)	1.06 (1.03)

[a] Yields of polymers were nearly quantitative in each case. [b] Homopolymers were obtained at the first-stage polymerization. [c] M_n(calcd) = ([monomer] × (MW of monomer) × *f*/[initiator]) + MW of initiator; $f = 1$ or 2, corresponding to the functionality of the initiators. [d] The molecular weights of the block copolymers were determined by using the molecular weights of the homopolymers and the molar ratios of monomer units in the block copolymer analyzed by ^{1}H NMR. [e] M_w/M_n was obtained by SEC calibration using standard polystyrenes in THF solution.

Scheme 3



precipitate as the reaction proceeded. After quenching the reaction with degassed methanol, the polymer was obtained by precipitation into degassed water. In the ^{1}H NMR spectrum (CD_3OD) of the polymer after the deprotection, the signal due to the oxymethyleneoxy group of the acetal linkage at 5.8 ppm completely disappeared. Figure 2 shows the ^{13}C NMR spectra of the polymer before deprotection (A) and after deprotection (B). As can also be seen clearly, the signals corresponding to the methylene carbon of the OCH_2O group at 100.7 ppm is not observed at all and the splitting of the aromatic carbon signals changed largely after deprotection. In the IR spectrum, the characteristic absorptions at 1039 and 1244 cm^{-1} due to the O–C–O linkage disappeared and alternatively the new stretching absorption corresponding to the catechol OH functionality appeared at 2500–3500 cm^{-1} for the deprotected polymers. The quantitative cleavage of the acetal blocking group for the starting poly(**1**) is thus obvious as indicated by the ^{1}H and ^{13}C NMR and IR spectroscopies.

As an additional evidence for the deprotection, the solubility of the resulting polymer after reaction drastically changed from that of the starting poly(**1**). The poly(**1**) was soluble in benzene, chloroform, THF, and 1,4-dioxane but insoluble in methanol, hexane, and water, while the poly(4-vinylcatechol) obtained by the deprotection was soluble in methanol, THF, DMF, and 1,4-dioxane but insoluble in hexane, benzene, chloroform, and water. The deprotected polymer containing the catechol moiety was not stable for a long period under exposure to air as previously suggested.[11b] Thus, the poly(4-vinylcatechol) was initially soluble, but it began to be colored and became insoluble in all the solvents as mentioned above.

However, even just after the deprotection, attempts to analyze the soluble sample of poly(4-vinylcatechol) by SEC in THF and DMF were unsuccessful. The polymer could not be eluted from the SEC columns probably due to the adsorption of the polar catechol moiety on the polystyrene gel column. Therefore, the hydroxy groups of the poly(4-vinylcatechol) were silylated or methylated by treating with *tert*-butyldimethylsilyl chloride or diazomethane (Scheme 4). Both

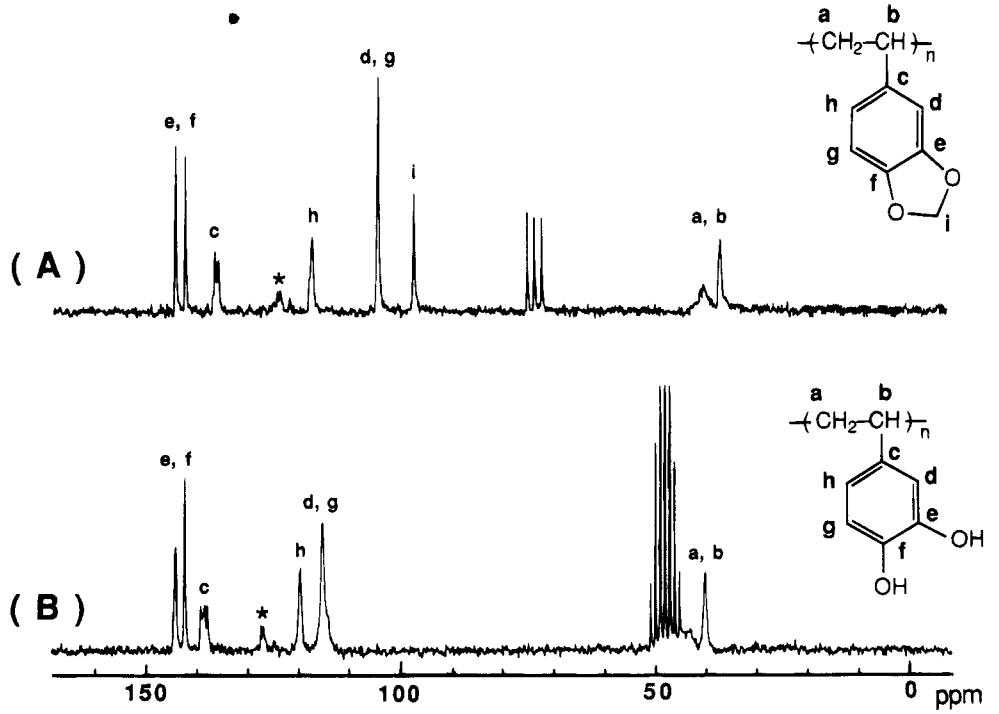
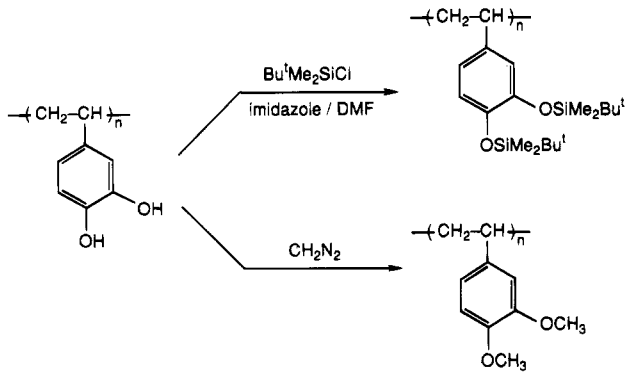


Figure 2. ^{13}C NMR spectra of poly(**1**) in $CDCl_3$ (A) and of poly(4-vinylcatechol) in CD_3OD (B). The signals due to the oligo(α-methylstyrene) of the initiator residue are marked with an asterisk.

Scheme 4



reactions toward two OH functions were found to proceed nearly quantitatively to give poly[3,4-bis((*tert*-butyldimethylsilyl)oxy)styrene] and poly(3,4-dimethoxystyrene). We measured again these purposefully modified polymers by SEC. Unfortunately, the SEC of these etherified polymers always showed multimodal curves with broad molecular weight distributions. For example, the polydispersity index of the poly(3,4-dimethoxystyrene) became broader (M_w/M_n = 1.41) after deprotection from that before deprotection (M_w/M_n = 1.05) as can be seen in Figure 3. The shoulders on the higher molecular weight side in the chromatogram apparently indicate that some intermolecular side reaction between polymers occurred during the course of either the deprotection or the methylation (and the silylation) reaction. The deprotection reaction under milder conditions (at room temperature for shorter time) resulted in an incomplete deprotection of the acetal linkage. Some modification or greater care of the workup is required to obtain a poly(4-vinylcatechol) of narrow molecular weight distribution.

The poly(**1**) and poly(**2**) were white powders and could be cast into transparent films from their solutions. The glass transition temperatures (T_g's) of poly(**1**) and poly(**2**), measured by differential scanning calorimetry (DSC), were 138 and 119 °C, respectively.

Experimental Section

Materials. Piperonal, 2,3-dihydroxybenzaldehyde, diiodomethane, imidazole, and *tert*-butyldimethylsilyl chloride were used without purification. α-Methylstyrene and styrene were distilled over calcium hydride. These styrenes were further purified by distillation in the presence of phenylmagnesium chloride on a vacuum line. THF used as a polymerization solvent was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and finally through a vacuum line from the sodium naphthalenide solution. Boron tribromide–methyl sulfide complex was prepared according to the literature.[13,14] The resulting powder of the complex was dissolved in methylene dichloride and stored under a nitrogen atmosphere. Diazomethane was prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide according to the previous report.[15]

Initiators. Commercially available *n*-BuLi and *sec*-BuLi were used without purification and they were diluted with dry *n*-heptane. Metal naphthalenides were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal in THF. The oligo(α-methylstyryl)-dilithium, -disodium, and -dipotassium were freshly prepared just prior to polymerizations from the corresponding metal naphthalenides and a 2–4 M quantity of α-methylstyrene at 20 °C for 1 min and then at −78 °C for 10 min. The corresponding monofunctional lithium salt was prepared by the reaction of *sec*-BuLi and a 2–4 M quantity of α-methylstyrene at −78 °C. These initiators were stored in ampules equipped with breakseals. The concentrations of initiators were determined by a colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum.[2b]

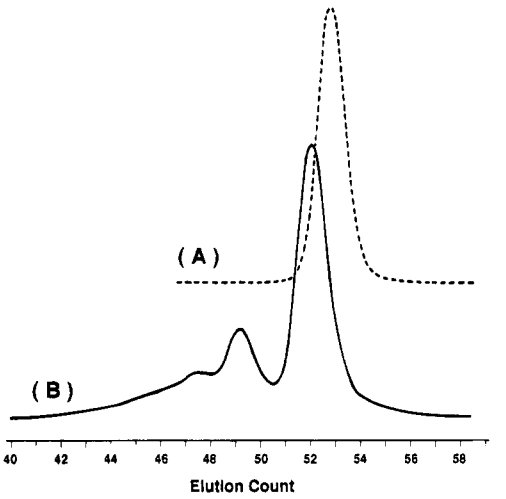


Figure 3. SEC curves of poly(**1**) before deprotection (A) and of poly(3,4-dimethoxystyrene) obtained after the deprotection and the subsequent methylation of the poly(**1**) (B): peak A, M_w/M_n = 1.05; peak B, M_w/M_n = 1.41.

5-Vinyl-1,3-benzodioxole (1). To a mixture of methyltriphenylphosphonium bromide (37.5 g, 150 mmol) and potassium *tert*-butoxide (21.3 g, 190 mmol), 80 mL of dry THF was added at room temperature under nitrogen. To this reaction mixture, piperonal (15.0 g, 100 mmol) in dry THF (40 mL) was added dropwise for 20 min under cooling in an ice bath. After stirring for 10 min at 0 °C, the reaction mixture was poured into cooled water, and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. After evaporation, the concentrated organic layer was poured into a large amount of hexane to precipitate triphenylphosphine oxide. After filtration, the filtrate was concentrated and purified by flash chromatography (hexane). After evaporation of hexane, the residue was distilled under vacuum to give a colorless liquid of **1** (10.3 g, 70 mmol, 70%, bp 58.6–60.0 °C/0.8 mmHg (lit.[11b] bp 50.5–51.0 °C/0.25 mmHg)): 90 MHz ^{1}H NMR ($CDCl_3$) δ 5.12 and 5.56 (2d, J = 11 and 17 Hz, CH_2=), 5.95 (s, 2H, OCH_2O), 6.63 (dd, 1 H, −CH=), 6.78–6.97 (m, 3H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 101.1 (OCH_2O), 105.5 (Ar, C2), 108.2 (Ar, C5), 112.0 (vinyl, CH_2=), 121.0 (Ar, C6), 132.3 (Ar, C6), 136.5 (vinyl, −CH=), 147.5 (Ar, C4), 148.1 (Ar, C3); IR (neat, cm^{-1}) 2892 (O−CH_2−O), 1629, 1489, 1249, 1041 (C−O−C), 988, 914. Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.76; H, 5.36.

4-Formyl-1,3-benzodioxole.[16] A mixture of 2,3-dihydroxybenzaldehyde (24.83 g, 180 mmol), diiodomethane (78.9 g, 295 mmol), K_2CO_3 (76.62 g, 554 mmol), copper(II) oxide (2.59 g, 33 mmol), and DMF (220 mL) was heated to 100–110 °C for 4.5 h under nitrogen. After cooling, the reaction mixture was poured into water (1 L) and extracted twice with diethyl ether. The organic phase was washed with 5% hydrochloric acid and water and then dried with anhydrous $MgSO_4$. After concentration, the two fractional distillations gave a liquid of 4-formyl-1,3-benzodioxole (15.35 g, 102 mmol, 57%, bp 111–112 °C/6 mmHg): 90 MHz ^{1}H NMR ($CDCl_3$) δ 6.14 (s, 2H, OCH_2O), 6.83–7.34 (m, 3H, Ar), 10.12 (s, 1H, CHO); 23 MHz ^{13}C NMR ($CDCl_3$) δ 102.5 (OCH_2O), 113.3 (Ar, C7), 119.4 (Ar, C4), 121.0 (Ar, C6), 121.7 (Ar, C5), 148.9 and 149.2 (Ar, C8 and C9), 187.8 (CHO); IR (neat, cm^{-1}) 1686 (CHO), 1630, 1459, 1265, 1233, 1058, 924, 777.

4-Vinyl-1,3-benzodioxole (2). **2** was synthesized by the reaction of 4-formyl-1,3-benzodioxole (6.20 g, 41 mmol), methyltriphenylphosphonium bromide (15.58 g, 44 mmol), and potassium *tert*-butoxide (9.63 g, 86 mmol) by a method similar to that in the case of **1**. After a similar purification by flash chromatography (hexane) and concentration, the residue was distilled under vacuum to give a colorless liquid of **2** (4.73 g,

32 mmol, 78%, bp 62–64.5 °C/1.5 mmHg (lit.[11b] 116 °C/1 mmHg)): 90 MHz ^{1}H NMR ($CDCl_3$) δ 5.37 and 5.89 (2d, 2H, J = 11 and 17 Hz, CH_2=), 5.99 (s, 2H, OCH_2O), 6.68 (dd, 1H, –CH=), 6.65–6.90 (m, 3H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 100.9 (OCH_2O), 107.7 (Ar, C7), 116.9 (vinyl, CH_2=), 120.3 and 120.5 (Ar, C4 and C5), 121.6 (Ar, C6), 131.2 (vinyl, –CH=), 145.1 (Ar, C9), 147.7 (Ar, C8); IR (neat, cm^{-1}) 2893 (OCH_2O), 1454, 1414, 1247, 1197, 1051 (C–O–C), 932, 916, 782, 730. Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.57; H, 5.54.

Purification. After careful fractional distillations, the purified monomers were sealed in a glass apparatus equipped with a breakseal under vacuum (10^{-6} mmHg). In order to remove impurities of the monomers (30 mmol), phenylmagnesium chloride (1 mmol) in THF was added and stirred at room temperature for 30 min. From the resulting solutions, the monomers were distilled on the vacuum line and then diluted with dry THF in the sealed all-glass apparatus equipped with breakseals. The resulting monomer solutions (0.5–0.7 M in THF) were stored at –30 °C until ready to use for the anionic polymerizations.

Polymerization Procedures. All polymerizations were carried out at low temperature (mainly at –78 °C) with shaking under high-vacuum conditions in an all-glass apparatus equipped with breakseals as previously reported.[2b] The polymerizations were quenched with degassed methanol. The reaction mixtures were poured into a large excess of methanol to precipitate the polymers. Polymers collected by filtration were purified by reprecipitation twice with a THF–methanol system and then by freeze-drying from benzene. Poly(**1**) and poly(**2**) thus obtained were characterized by ^{1}H and ^{13}C NMR and IR spectroscopies. The following is the full list.

Poly(1): 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.7–2.4 (3H, CH_2CH), 5.9 (2H, OCH_2O), 5.4–6.7 (overlapping, 3H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 39–46 (CH_2CH), 100.7 (OCH_2O), 107.7 (Ar, C4 and C7), 120.7 (Ar, C6), 139.0 (Ar, C5), 145.5 (Ar, C8), 147.5 (Ar, C9); IR (KBr, cm^{-1}) 3100–2700, 1505, 1484, 1440, 1244, 1040, 937, 808.

Poly(2): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.0–2.5 (m, 3H, CH_2-CH), 5.5 (2H, OCH_2O), 5.8–6.7 (m, 3H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 36–42 (CH_2CH), 100.1 (OCH_2O), 106.0 (Ar, C7), 120.9 (Ar, C5 and C6), 127.4 (Ar, C4), 145.2 (Ar, C9), 146.9 (Ar, C8); IR (KBr, cm^{-1}) 3100–2700, 1636, 1596, 1478, 1355, 1250, 1056, 939, 909, 831, 773, 728.

Typical Procedure of Block Copolymerization. In an all-glass apparatus in vacuo, the first-stage polymerization of **1** (3.26 mmol) was initiated with oligo(α-methylstyryl)dilithium (0.0920 mmol) in THF at –78 °C. After 0.5 h, a small portion of the living prepoly(**1**) (0.0224 mmol) was withdrawn to determine the characteristics of the first-stage polymer. To the residue of polymerization system, styrene (4.35 mmol) in THF was added in one portion with vigorous stirring and reacted for 10 min to complete the second-stage polymerization. After quenching with degassed methanol, both polymers were obtained in quantitative yield. Both the homopoly(**1**) and the poly(styrene-*b*-**1**-*b*-styrene) possessed predicted molecular weights and narrow molecular weight distributions as shown in Table 2.

Deprotection of Poly(1). Poly(**1**) (0.30 g, 2.0 mmol based on monomer unit) was dissolved in 1,2-dichloroethane (30 mL) under nitrogen. To this solution a 1 M methylene dichloride solution of boron tribromide–methyl sulfide complex (4 mL, 4 mmol) was added.[13,14] The reaction mixture was refluxed for 4.5 h and then cooled to room temperature. To quench the reaction, 3 mL of methanol was added to the reaction mixture, and the solvent was removed by evaporation. The residue was redissolved in methanol, and the resulting solution was poured into degassed water to precipitate a polymer. The precipitated polymer was filtered and immediately dried under vacuum. The resulting polymer was characterized by ^{1}H and ^{13}C NMR and IR spectroscopies. **Poly(4-vinylcatechol):** 90 MHz ^{1}H NMR (CD_3OD) δ 0.5–2.2 (m, 3 H, CH_2CH), 5.8–7.2 (3H, Ar), signals of the catecholic OH were not observed due to proton exchange in CD_3OD; 23 MHz ^{13}C NMR (CD_3OD) δ 40–45 (CH_2-CH), 116.3 (Ar, C3 and C6), 120.6 (Ar, C5), 140.2 (Ar, C4), 143.3 and 145.3 (Ar, C1 and C2); IR (KBr, cm^{-1}) 3500–2500 (OH), 1608, 1521, 1443, 1368, 1281, 1111, 812, 782.

Silylation of Poly(4-vinylcatechol). A mixture of poly(4-vinylcatechol) (0.10 g, 0.7 mmol based on monomer unit), imidazole (0.23 g, 3.4 mmol), *tert*-butyldimethylsilyl chloride (0.27 g, 1.82 mmol), and DMF (5 mL) was stirred at room temperature for 18 h under nitrogen. The reaction mixture was quenched with 5% sodium hydroxide solution and extracted with hexane. After concentration, the residue was poured into methanol to precipitate a silylated polymer (0.23 g). The resulting polymer was then characterized by ^{1}H and ^{13}C NMR and IR spectroscopies. 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.1 (12H, $SiCH_3$), 0.9 (18H, $C(CH_3)_3$), 0.6–2.1 (overlapping, 3H, CH_2CH), 5.0–6.7 (3H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ –3.9 ($SiCH_3$), 18.5 ($C(CH_3)_3$), 26.2 ($C(CH_3)_3$), 39–43 (CH_2CH), 114, 120, 127, 140, 144, and 147 (Ar); IR (KBr, cm^{-1}) 2955, 2930, 2859, 1506, 1286, 1255 ($SiCH_3$), 1123, 905 (Si–O–C), 838, 782.

Methylation of Poly(4-vinylcatechol). To a suspension of poly(4-vinylcatechol) (0.07 g, 0.5 mmol based on monomer unit) in benzene (10 mL), diazomethane[15] (8 mmol) in ether (20 mL) was added in small portions at room temperature. As the methylation proceeded, the polymer dissolved into the solution. The yellow solution was kept overnight at room temperature. After quenching the reaction with acetic acid, the reaction mixture was concentrated by evaporation and poured into methanol to precipitate a polymer (0.09 g). 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.0–2.3 (3H, CH_2CH), 3.6 and 3.8 (broad, 6H, OCH_3), 5.7–7.1 (3H, Ar).

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^{1}H, and 22.53 MHz ^{13}C) in $CDCl_3$ or in CD_3OD. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) or CD_3OD (δ 49.0) for ^{13}C NMR as standard. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. Size exclusion chromatograms (SEC) for MWD determination were obtained at 40 °C with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H_{XL}, G4000H_{XL}, and G3000H_{XL}) with ultraviolet (254 nm) or refractive index detection. THF was a carrier solvent at a flow rate of 1.0 mL min^{-1}. Vapor pressure osmometry (VPO) measurements for number-average molecular weight determination were made with a Corona 117 instrument in benzene solution. The glass transition temperatures of the polymers were measured by differential scanning calorimetry using a Seiko Instruments DSC220 apparatus and analyzed by a SSC5200TA station. The samples were first heated to 250 °C, cooled rapidly to –20 °C, and then scanned again at a rate of 20 °C/min.

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References and Notes

(1) For a review, see: Nakahama, S.; Hirao, A. *Prog. Polym. Sci.* **1990**, *15*, 299. For a recent publication of this series, see ref 7d.
(2) (a) Hirao, A.; Yamaguchi, K.; Takenaka, K.; Suzuki, K.; Nakahama, S.; Yamazaki, N. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 941. (b) Hirao, A.; Takenaka, K.; Packrisamy, S.; Yamaguchi, K.; Nakahama, S. *Makromol. Chem.* **1985**, *186*, 1157. (c) Hirao, A.; Kitamura, K.; Takenaka, K.; Nakahama, S. *Macromolecules* **1993**, *26*, 4995.
(3) Hirao, A.; Shione, H.; Wakabayashi, S.; Nakahama, S.; Yamaguchi, K. *Macromolecules* **1994**, *27*, 1835.
(4) (a) Yamaguchi, K.; Hirao, A.; Suzuki, K.; Takenaka, K.; Nakahama, S.; Yamazaki, N. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 395. (b) Suzuki, K.; Yamaguchi, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2607.
(5) (a) Hirao, A.; Ishino, Y.; Nakahama, S. *Makromol. Chem.* **1986**, *187*, 141. (b) Hirao, A.; Nakahama, S. *Macromolecules* **1987**, *20*, 2968. (c) Ishizone, T.; Kato, R.; Ishino, Y.; Hirao, A.; Nakahama, S. *Macromolecules* **1991**, *24*, 1449. (d) Ishizone, T.; Sueyasu, N.; Sugiyama, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1993**, *26*, 6976.
(6) Hirao, A.; Kato, K.; Nakahama, S. *Macromolecules* **1992**, *25*, 535.

(7) (a) Ishino, Y.; Hirao, A.; Nakahama, S. *Macromolecules* **1986**, *19*, 2307. (b) Hirao, A.; Ishino, Y.; Nakahama, S. *Macromolecules* **1988**, *21*, 561. (c) Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2895. (d) Ishizone, T.; Kurosawa, H.; Hirao, A.; Nakahama, S. *Macromol. Chem. Phys.* **1994**, *195*, 3173.
(8) (a) Ishizone, T.; Hirao, A.; Nakahama, S.; Kakuchi, T.; Yokota, K.; Tsuda, K. *Macromolecules* **1991**, *24*, 5230. (b) Tsuda, K.; Ishizone, T.; Hirao, A.; Nakahama, S.; Kakuchi, T.; Yokota, K. *Macromolecules* **1993**, *26*, 6985.
(9) Cassidy, H. G. *J. Polym. Sci., Part D* **1972**, *6*, 1.
(10) (a) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786, 6456. (b) Iwabuchi, S.; Nakahira, T.; Fukushima, Y.; Saito, O.; Kojima, K. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 785.
(11) (a) Daly, W. H.; Chotiwana, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1981**, *22* (1), 164. (b) Daly, W. H.; Moulay, S. *J. Polym. Sci., Polym. Symp.* **1986**, *74*, 227.
(12) For examples see: (a) Ranade, A. C.; Mali, R. S.; BVhide, S. R.; Mehta, S. R. *Synthesis* **1976**, 123. (b) Conrad, P. C.; Kwiatkowski, P. L.; Fuchs, P. L. *J. Org. Chem.* **1987**, *52*, 586. (c) Bengtsson, S.; Högberg, T. *J. Org. Chem.* **1989**, *54*, 4549.
(13) Williard, P. G.; Fryhle, C. B. *Tetrahedron Lett.* **1980**, *21*, 3731.
(14) Brown, H. C.; Ravindan, N. *Inorg. Chem.* **1977**, *16*, 2938.
(15) De Boer, Th. J.; Backer, H. J. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 229.
(16) Smidrkal, J. *Collect. Czech. Chem. Commun.* **1982**, *47*, 2140.

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