Protection and Polymerization of Functional Monomers. 25.[1] Synthesis of Well-Defined Polystyrene Bearing a Triol Functionality by Means of Anionic Living Polymerization of 4-[(4-(4-Vinylphenyl)butoxy)methyl]-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane

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ABSTRACT: Anionic polymerization of 4-[(4-(4-vinylphenyl)butoxy)methyl]-1-methyl-2,6,7-trioxabicyclo-[2.2.2]octane (**3**) was carried out in THF at −78 °C for 10 min with oligo(α-methylstyryl)lithium, -dilithium, -potassium, and -dipotassium. Poly(**3**) was quantitatively obtained in each case, and the resulting polymers possessed predicted molecular weights and narrow molecular weight distributions (M_w/M_n < 1.1), indicating the living character of the polymerization of **3**. By the sequential anionic copolymerization of **3** and styrene, well-defined block copolymers were successfully synthesized. The deprotection of poly(**3**) was performed by treating with 2 N HCl in THF for 30 min and subsequently with 10% NaOH(aq) in MeOH for 30 min. The bicyclic ortho ester moiety of poly(**3**) was completely cleaved to give a poly[2-(((4-(4-vinylphenyl)butyl)oxy)methyl)-2-(hydroxymethyl)-1,3-propanediol] bearing three hydroxyl groups in each monomer unit.

Introduction

Since our first successful synthesis of a well-defined poly(4-vinylphenol) via the anionic living polymerization of 4-((*tert*-butyldimethylsilyl)oxy)styrene in 1982,[2a] protection and anionic living polymerization of functional monomers has become a prominent method to synthesize functional polymers with precisely regulated chain lengths as well as well-defined novel block copolymers with functional segments. We have synthesized a series of polystyrenes and their block copolymers with functional groups including OH,[2] NH_2,[3] SH,[4] CHO,[5] COOH,[6] $COCH_3$,[7] and C≡CH.[8]

Recently, we have systematically prepared a variety of hydroxy group containing polymers by this methodology, since hydroxy groups are interesting from the viewpoints of their reactivity, hydrophilicity, and potential for forming hydrogen bonds and chelation to metal ions. The polymers synthesized are poly(3- and 4-vinylphenol)s, poly[(3-hydroxymethyl)styrene], poly-[2-, 3-, and 4-(2-hydroxyethyl)styrene]s,[2] poly(2-hydroxyethyl methacrylate),[9] and poly(2,3-dihydroxypropyl methacrylate).[10] They are the polystyrenes with phenolic or alcoholic functionalities at different substituted positions and polymethacrylates with one or two hydroxy groups per monomer unit, possessing predicted molecular weights and narrow molecular weight distributions. All of these polymers could be synthesized by the anionic living polymerizations of monomers bearing suitably protected OH functionalities. Selection of the protecting groups was critical for the perfect protection of the functional group during the polymerization reaction and their facile deprotection. Very interesting amphiphilic block copolymers containing the above-mentioned polymer segments have been also prepared. For example, the block copolymer of styrene and 2-hydroxyethyl methacrylate has been found to show excellent nonthrombogenic activity[11] when compared with the commercially available "Biomer" made of the segmented polyurethane. Characteristic reconstruction of the top surface microdomains of some block copolymers can be observed in response to environmental change from dry air to water and from water to dry air.[12]

As an extension of these studies, we here address a simple triol as a functionality which was expected to afford higher hydrophilicity and/or polarity relative to the parent polymers, in addition to the ability to form tridentate chelates. We report the synthesis of polystyrenes with triol functionality in each monomer unit, by the method of protection and anionic living polymerization of styrene monomers with the triol protected by the form of 2,6,7-trioxabicyclo[2.2.2]octane. The focuses of this work are the protective ability of this bicyclic ortho ester for the triol moiety under the conditions of the anionic living polymerization of styrene derivatives, and the facility with which the triol function can be regenerated without damage to the polymer chain.

Results and Discussion

The key to the methodology described in the Introduction involves a choice of protecting groups which should be completely stable under the conditions of anionic living polymerization but readily removed under conditions mild enough not to damage the polymer chain. Through our previous work on the anionic living polymerizations of the protected monomers, most of the hydroxy groups of vinylphenols, hydroxymethyl- and (2-hydroxyethyl)styrenes, and 2-hydroxyethyl methacrylate were satisfactorily masked with trialkylsilyl groups.[2] Recently, acetals were found to work successfully as alternative protecting groups for hydroxy groups during the anionic living polymerization of styrene[5c] and methacrylate derivatives.[10]

Among candidates for the protecting groups of a triol, we selected 2,6,7-trioxabicyclo[2.2.2]octane, a bicyclic ortho ester, to protect the triol moiety of styrene derivatives. As suggested in previous literature,[13–17]

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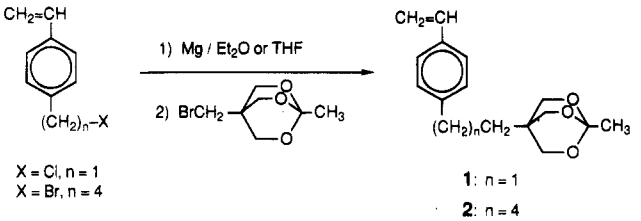
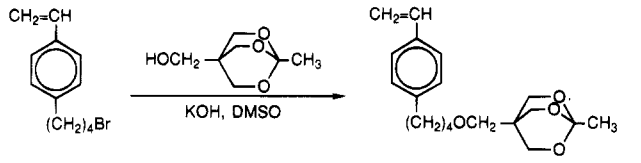
Scheme 1



Scheme 2



this bicyclic ortho ester was expected to be stable to the highly reactive organolithium compounds often used as anionic initiators. It is also well-known that bicyclic ortho esters can be easily cleaved to regenerate the triol functionality under mild conditions.[15,18,19] An additional synthetic advantage of these bicyclic ortho esters is that three hydroxy groups in the monomer can be masked simultaneously. Very recently, we have also ascertained the stability of the ortho ester function toward anionic living polystyrene in the reaction of anionic living polystyrene with 4,4,4-trimethoxy-1-bromobutane; the ortho ester in this case was used for the protection of a carboxylic acid.[20] The highly reactive terminal carbanion does not attack the ortho ester function but the C–Br center by nucleophilic substitution.

Synthesis of Monomers. At the beginning of this study, we attempted to synthesize two novel styrene derivatives, **1** and **2**, in which the bicyclic ortho ester was separated from the styrene framework by two or five methylene groups. They were directly synthesized by the coupling reactions of the corresponding Grignard reagents and 4-(bromomethyl)-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane, as shown in Scheme 1. Unfortunately, we could not obtain sufficient amounts of the purified monomers for the anionic polymerization, since significant degradation of the ortho ester function occurred during the synthesis and the isolation step of **1** and **2**. Only one attempt of the anionic polymerization of **2** could be performed, at a low monomer to initiator ratio ([M]/[I] = 7.7) with cumylpotassium in THF at −78 °C for 30 min. The polymerization system showed a characteristic red coloration which resembled that of the anionic living polystyrene. After termination with methanol, a polymer was quantitatively obtained. In the SEC analysis, the polymer was found to possess a relatively narrow molecular weight distribution (M_w/M_n = 1.17) and eluted at a reasonable molecular weight region based on the calculated value. The results support living polymerization of **2** under the anionic conditions employed here.

Monomer **3**, in which the ortho ester is attached to the styrene framework via an ether linkage, was easily prepared in good yield (65%) by a Williamson ether synthesis of 4-(4-bromobutyl)styrene and 4-(hydroxymethyl)-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane (Scheme 2). This monomer could be readily purified by flash column chromatography and subsequent recrystallization from either methanol or hexane and was stable for a long period of exposure to air. Thus, **3** became the monomer of choice for this study.

Table 1. Anionic Polymerization of 3 in THF at −78 °C for 10 min[a]

run	amt of **3** mmol	amt of initiator, mmol	amt of α-MeSt,[b] mmol	$10^{-3} M_n$ calcd[c]	$10^{-3} M_n$ obsd[d]	M_w/M_n[e]
1	1.72	*s*-BuLi, 0.0949	0.367	6.3	6.2	1.07
2	0.684	*s*-BuLi, 0.0303	0.375	8.3	10	1.06
3	2.26	*s*-BuLi, 0.0293	0.470	27	24	1.04
4	1.23	Li-Naph,[f] 0.0518	0.463	18	16	1.09
5	1.75	Cumyl-K,[g] 0.0858	0.232	6.9	6.9	1.09
6	1.62	Cumyl-K, 0.0677	0.285	8.5	8.0	1.16
7	1.50	K-Naph,[h] 0.0843	0.512	13	15	1.15

[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] Cumylpotassium. [h] Potassium naphthalenide.

Anionic Polymerization of 3. Anionic polymerization of **3** was carried out in THF at −78 °C for 10 min. The initiators were the monofunctional and difunctional living anionic oligomers of α-methylstyrene associated with either the lithium or potassium countercation. The polymerization of **3** always showed characteristic orange (Li^+) or red (K^+) coloration during the course of the reaction, indicating the existence of the propagating polystyryl carbanions in both polymerization systems. These colors immediately disappeared upon the addition of a small amount of degassed methanol, to terminate the polymerizations. The reaction system was then poured into a large excess of methanol to precipitate the polymer, which was subsequently characterized by ^1H and ^{13}C NMR and IR spectroscopies. On the basis of these analyses, it was found that the vinyl polymerization of **3** occurred exclusively, and no cleavage of bicyclic ortho ester was observed.

Table 1 shows the polymerization results of **3** with various initiators at −78 °C in THF. All the polymerizations of **3** were complete within 10 min, and the polymers could be obtained in quantitative yield. The number-average molecular weights of the poly(**3**)s measured by vapor pressure osmometry (VPO) agreed well with the calculated values from the molar ratios of monomer to employed initiators. Moreover, the size exclusion chromatography (SEC) traces of the resulting poly(**3**)s always showed unimodal and narrow distributions (M_w/M_n = 1.04−1.15), suggesting that the rapid initiation reaction of **3** occurred with the living oligomers of α-methylstyrene.

In addition to the persistency of the propagating chain end of poly(**3**), which will be shown in the later section of the block copolymerization, the results obtained here substantiate the living character of the anionic polymerization of **3**. Obviously, the bicyclic ortho ester protecting moiety is stable enough to give a living polymer derived from **3**, a novel styrene derivative bearing three masked OH groups, under the anionic conditions used here.

Block Copolymerization of 3 with Styrene. Generation of the living polymer from **3** enables us to synthesize novel block copolymers having predictable main chain architecture. The results of block copolymerization also provide information concerning the stability of the propagating species as well as the reactivity of the monomers and the living polymers. At first, the sequential polymerization of **3** (first monomer) and styrene (second monomer) was carried out with oligo(α-methylstyryl)lithium in THF at −78 °C in order

Table 2. Block Copolymerization of 3 with Styrene at −78 °C in THF[a]

			block copolymer (homopolymer[b])		
			$10^{-3} M_n$		
run	first monomer	second monomer	calcd[c]	obsd[d]	M_w/M_n[e]
8	**3**	styrene	15 (6.3)	18 (6.2)	1.06 (1.07)
9	styrene	**3**	15 (8.8)	18 (11)	1.07 (1.07)

[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)/[initiator] + MW of initiator. [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.

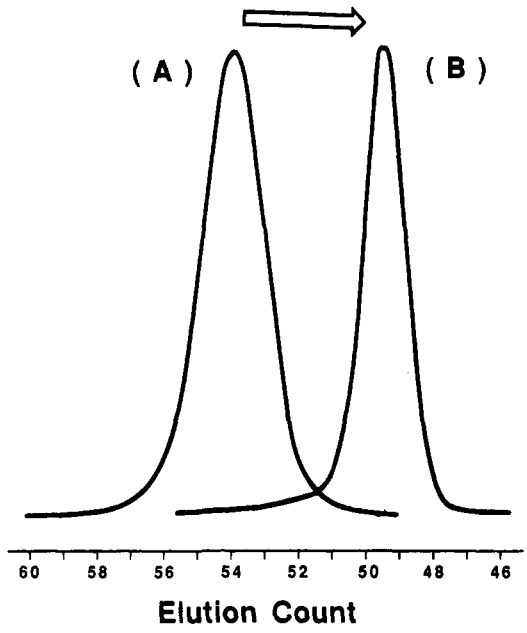


Figure 1. SEC curves of poly(**3**) at the first-stage polymerization (A) and of poly(**3**-*b*-styrene) obtained at −78 °C (B) (Table 2, run 8): peak A, M_n(obsd) = 6200, M_w/M_n = 1.07; peak B, M_n(obsd) = 18 000, M_w/M_n = 1.06. (The second monomer was added 20 min after the first-stage polymerization.)

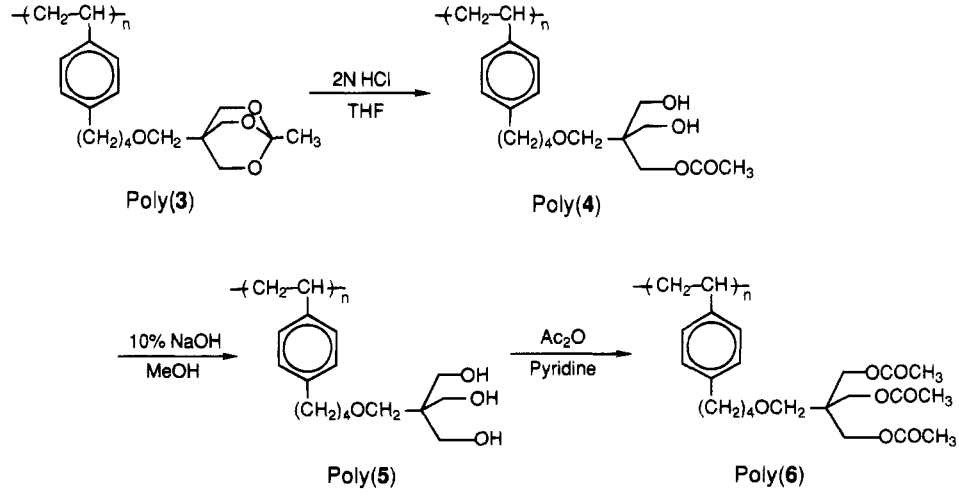
to synthesize a block copolymer. After completion of the first-step polymerization of **3** for 20 min, styrene was added to the reaction system. A change of coloration from orange to dark yellow and an increase of the viscosity were immediately observed. After termination, the copolymer was obtained quantitatively. The composition of each polymer segment in the copolymer was determined by ^{1}H NMR spectroscopies and agreed well with the feed ratio of **3** and styrene. The observed molecular weights of the prepolymer and the copolymer were fairly consistent with the calculated values, as shown in Table 2 (run 8). Moreover, the SEC curve of the copolymer completely shifted toward the higher molecular weight side after the addition of styrene, in keeping with the narrow molecular weight distribution of the polymer (M_w/M_n = 1.06, Figure 1). These results show clearly that the active chain end of poly(**3**) can initiate the second-stage polymerization of styrene to afford a well-defined AB diblock copolymer, poly(**3**-*b*-styrene), with near quantitative efficiency. Thus, it is evident that the propagating carbanion derived from **3** is stable at −78 °C, at least after 20 min of polymerization.

By changing the addition order of the monomers, a BA type block copolymer of reversed sequence was similarly synthesized (run 9). The results of the two block copolymerizations support the view that the so-called "reversible" block copolymerization is possible between **3** and styrene and the anionic polymerizability of **3** is similar to that of styrene. After complete deprotection of the poly(**3**) segment, block copolymers of **3** and styrene can be converted into the tailor-made amphiphilic block copolymers having hydrophilic poly(**5**) segments and hydrophobic polystyrene segments, as shown later.

Deprotection of Poly(3). It has thus been proven that the bicyclic ortho ester moiety is an excellent protecting group for the triol function of **5** under the conditions of anionic polymerization. The deprotection of the resulting poly(**3**) was carried out to liberate the three OH functionalities in two steps, as shown in Scheme 3.[15]

Acid Hydrolysis of Poly(3) (First Step). Poly(**3**) was treated with 2 N HCl in THF for 30 min at room temperature. After the reaction, the ^{1}H signals due to CH_3 (1.44 ppm) and $C(CH_2O)_3C$ (3.97 ppm) completely disappeared, and alternatively new signals of $COCH_3$ (3H, 2.03 ppm), CH_2OH (4H, 3.63 ppm), and CH_2OAc (2H, 4.14 ppm) were observed. The integral ratio of these signals indicated the quantitative transformation of poly(**3**) to poly(**4**), containing two OH groups and one acetate group, although the ^{1}H signal of the OH function could not be found, probably due to the proton exchange

Scheme 3



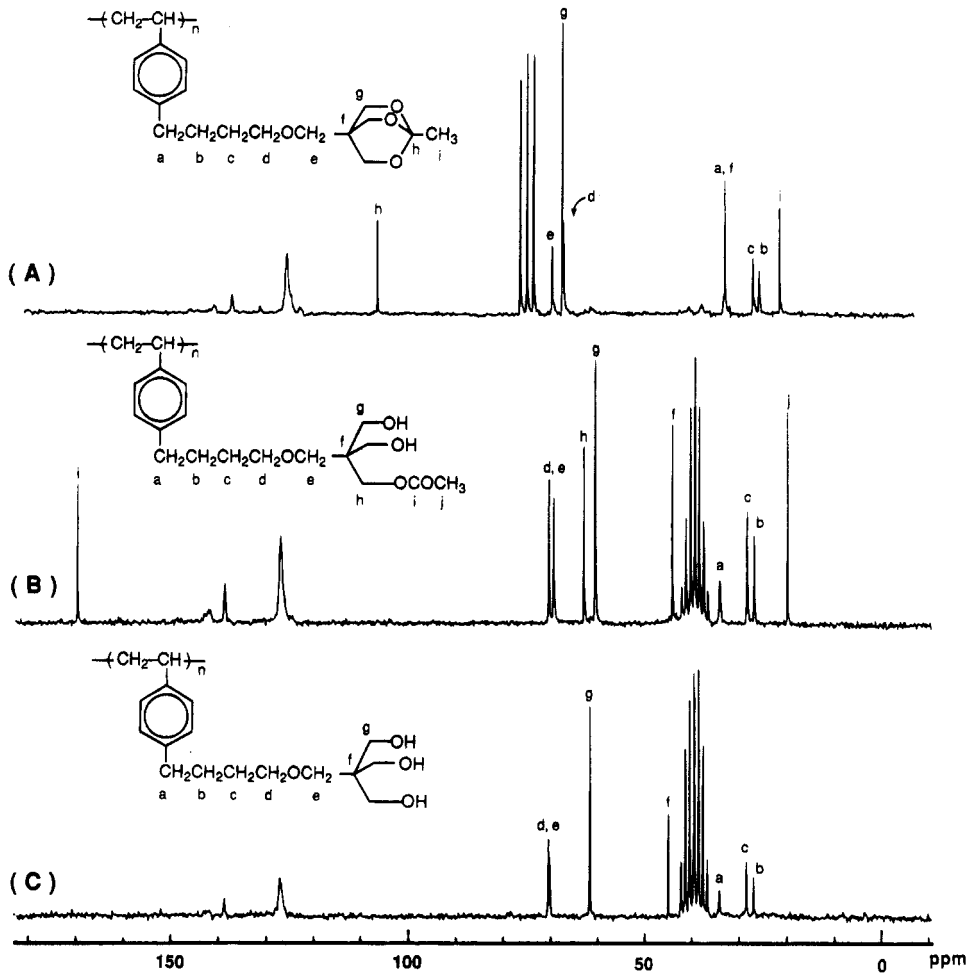


Figure 2. ^{13}C NMR spectra of poly(**3**) in $CDCl_3$ (A), poly(**4**) in DMSO-d_6 (B), and poly(**5**) in DMSO-d_6.

in CD_3OD. The change of the spectrum of the resulting polymer is also clearly observed in the ^{13}C NMR, as shown in Figure 2. The signals at 23.6 ppm (CH_3), 69.7 ppm ($C(CH_2O)_3C$), and 108.7 ppm ($C(CH_2O)_3C$) completely disappear, while the signals at 19.7 ppm ($COCH_3$), 60.7 ppm (CH_2OH), 63.1 ppm (CH_2OAc), and 170.9 ppm ($COCH_3$, carbonyl) appear. The IR spectrum after the reaction also changed significantly; for example, new strong characteristic absorptions of the ester C=O group at 1242 and 1739 cm^{-1} and a broad OH group absorption at 3200–3700 cm^{-1} appeared. Thus, the acid cleavage of the ortho ester in poly(**3**) proceeds quantitatively and poly(**4**) can be isolated as an intermediate polymer for poly(**5**) (Scheme 3).

Basic Saponification of Poly(4) (Second Step). The resulting poly(**4**) was next treated with 10% NaOH solution in MeOH/H_2O for 30 min at room temperature. In the ^1H NMR spectrum after the second-step reaction, the signals at 2.03 ppm ($COCH_3$) and 4.14 ppm (CH_2OAc) for poly(**4**) could not be observed, and the intensity of the signal at 3.63 ppm (CH_2OH) became stronger. The observed signal intensity of the spectrum agreed well with the expected values for poly(**5**). As can be seen clearly in Figure 2C, the ^{13}C NMR signals of poly(**4**) derived from the CH_2OAc groups at 19.7 ppm ($COCH_3$), 63.1 ppm (CH_2OAc), and 170.9 ppm ($COCH_3$) completely disappear and the single signal corresponding to the CH_2OH group is present at 61.7 ppm. The characteristic IR absorption of the carbonyl function at 1739 cm^{-1} was no longer present after the basic hydrolysis, and the strong absorption of three OH groups could be observed at 3200–3700 cm^{-1}. The complete removal of the acetyl group from poly(**4**) is evident from these spectroscopic observations. The resulting polymer is thus characterized as the expected poly(**5**), a polystyrene bearing three terminal CH_2OH groups in each monomer unit. The quantitative deprotection of the block copolymer of **3** and styrene similarly proceeded to give a tailored poly(**5**-*b*-styrene) of known chain architecture (Table 2, run 8).

Acetylation of Hydroxyl Groups of Poly(5). We attempted the SEC measurement of the deprotected polymer in order to check the molecular weight distribution after the acetylation of triol functionality due to the insolubility of poly(**5**) in THF. The spectroscopic information strongly supported the conclusion that acetylation of poly(**5**) proceeded quantitatively to afford poly(**6**), in which the three terminal CH_2OH groups in each monomer unit were converted into CH_2OAc moieties by reaction with acetic anhydride in pyridine at room temperature for 2 days (see Experimental Section). After reaction, the solubility of the polymer appreciably changed, and the resulting acetylated poly(**6**) was soluble in THF. Figure 3 shows the SEC traces (THF) of poly(**3**) before deprotection (A), poly(**4**) just after the first-step acid deprotection (B), and poly(**6**) after masking the polar OH functionalities by acetylation (C). The SEC curve of poly(**4**) shows a long tailing at the low molecular weight region, probably due to the adsorption of the polar OH functions on the SEC gel column during the size exclusion process in THF. Although we have not obtained the SEC curve of poly(**5**) because of its insolubility in THF, Figure 3C clearly shows that a unimodal and narrow molecular weight distribution of

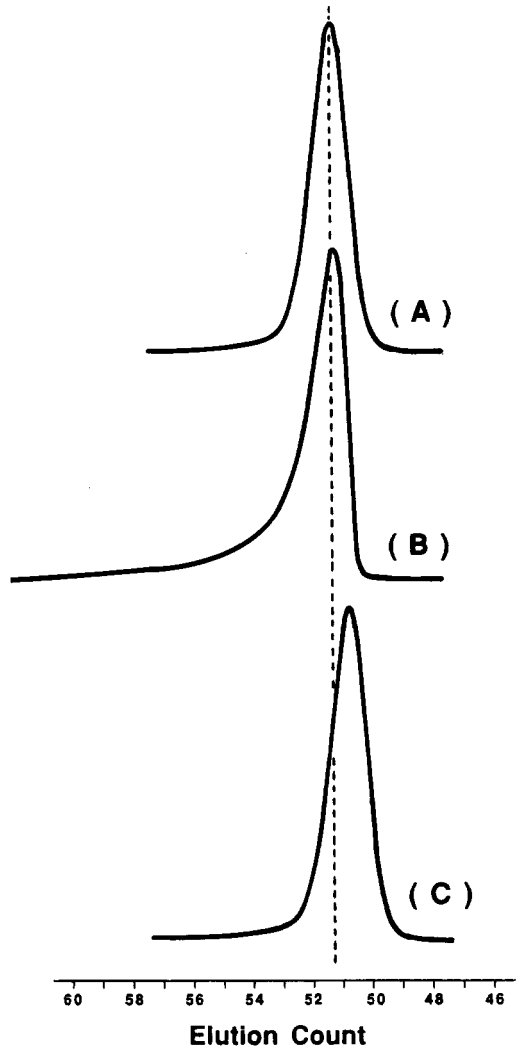


Figure 3. SEC curves of poly(**3**) before deprotection (A), poly(**4**) after the first-stage acid hydrolysis (B), and poly(**6**) after the acetylation of poly(**5**) (C): peak A, M_n(obsd) = 22 000, M_w/M_n = 1.04; peak C, M_n(obsd) = 25 000, M_w/M_n = 1.05.

the acetylated poly(**6**) is maintained (M_w/M_n = 1.05). The SEC trace of poly(**6**) slightly shifts toward the higher molecular weight region from that of the parent poly(**3**) (M_w/M_n = 1.04) without broadening of the distribution. It is clear from this observation that the two-step deprotection of poly(**3**) smoothly proceeds to give a well-defined poly(**5**) without undesirable side reactions such as cross-linking and chain degradation. Even after the three-step polymer reactions (acid hydrolysis, saponification, and acetylation), the resulting polymer apparently possesses a narrow molecular weight distribution, as expected. In addition, the attainment of the quantitative acetylation shows the high reactivity of all the OH groups in poly(**5**) under the conditions of the polymer reaction employed here.

The complete conversions of the polymer pendant groups were also supported by the drastic solubility change of the polymers throughout the three-step reactions. The solubilities of the resulting polymers are summarized in Table 3 with that of polystyrene as a reference. Before deprotection, poly(**3**) was soluble in nonpolar solvents such as benzene, diethyl ether, and chloroform and insoluble in polar solvents such as methanol and ethanol. In contrast, poly(**4**) became soluble in methanol and ethanol but insoluble in benzene, diethyl ether, and chloroform. The solvents of poly(**5**) having three OH groups were more limited

Table 3. Solubilities of the Resulting Polymers[a]

solvent	polymer				
	poly(**3**)	poly(**4**)	poly(**5**)	poly(**6**)	polystyrene
hexane	I	I	I	I	I
benzene	S	I	I	S	S
diethyl ether	S	I	I	I	S
ethyl acetate	S	S	I	S	S
chloroform	S	I	I	S	S
acetone	S	S	I	S	S
pyridine	S	S	S	S	S
1,4-dioxane	S	S	S	S	S
tetrahydrofuran	S	S	I	S	S
N,*N*-dimethylformamide	S	S	S	S	S
dimethyl sulfoxide	S	S	S	S	S
ethanol	I	S	S	I	I
methanol	I	S	S	I	I
water	I	I	I	I	I

[a] I, insoluble; S, soluble.

compared with the case of poly(**4**). Poly(**5**) was soluble only in the strong polar solvents such as DMF, DMSO, methanol, and ethanol and became insoluble in acetone, ethyl acetate, and even in THF, while unexpectedly it was not soluble in water. The solubility of the acetylated poly(**6**) resembled that of poly(**3**).

In conclusion, we have succeeded in carrying out the anionic living polymerization of **3**, a styrene derivative bearing a triol function protected by a bicyclic ortho ester moiety. Precise controls of the molecular weight and its distribution in poly(**3**) were attained. The persistency of the propagating carbanion of the living poly(**3**) could be demonstrated by sequential block copolymerization of **3** and styrene. Acid hydrolysis and subsequent basic saponification of the resulting poly(**3**) gave hydrophilic poly(**5**), with well-defined chain structures. This work demonstrates that the bicyclic ortho ester moiety is an excellent protecting group for the synthesis of polystyrene bearing a triol moiety, via anionic living polymerization and subsequent deprotection.

Experimental Section

Materials. 4-(Chloromethyl)styrene, kindly supplied from Seimi Chemical Co. Ltd., was used for the synthesis of monomer without purification. Pentaerythritol, orthoacetic acid triethyl ester, *p*-toluenesulfonic acid, 1,3-dibromopropane, and acetic anhydride were used without purification. Monobromopentaerythritol was synthesized in 34% yield by the reaction of pentaerythritol and 48% HBr according to the reported procedure.[18] A THF solution (0.1 M) of Li_2CuCl_4 was synthesized by the reaction of LiCl and $CuCl_2$ according to the literature.[21] α-Methylstyrene and styrene were distilled over calcium hydride. These styrene monomers were further purified by distillation in the presence of phenylmagnesium chloride (THF solution) 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 vacuum line from the sodium naphthalenide solution.

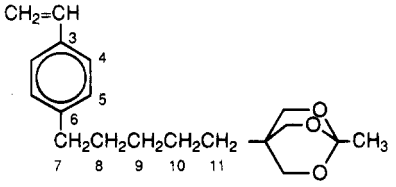
Initiators. Commercially available *s*-BuLi as a 1.05 M solution in cyclohexane was used without purification and diluted with *n*-heptane. Lithium naphthalenide and potassium naphthalenide were prepared by the reactions of a small excess amount of naphthalene with the corresponding alkali metal in dry THF. Cumylpotassium was prepared by the reaction of cumyl methyl ether and potassium–sodium alloy in dry THF. These initiators were stored at −30 °C in ampules equipped with breakseals. The difunctional oligo(α-methylstyryl)dilithium and -dipotassium were freshly prepared just prior to the 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

monofunctional oligo(α-methylstyryl)lithium was similarly prepared by the reaction of *s*-BuLi and a 2–4 M quantity of α-methylstyrene in THF at −78 °C for 30 min. The concentration of initiators was determined by colorimetric titration with standardized 1-octanol in a sealed reactor under high-vacuum conditions.[2b]

4-(4-Bromobutyl)styrene. To a stirred suspension of magnesium ribbon (5.72 g, 236 mmol) in dry ether (25 mL) was added 4-(chloromethyl)styrene (30.0 g, 197 mmol) in 100 mL of dry ether dropwise at 0 °C for 30 min. After complete consumption of 4-(chloromethyl)styrene, the reaction mixture was allowed to stand and the supernatant was transferred to a dropping funnel. To a mixture of 1,3-dibromopropane (73.3 g, 363 mmol), Li_2CuCl_4 (1.5 mmol),[21] and dry THF (235 mL) was added the ether solution of the Grignard reagent dropwise at 10 °C, and then the solution was stirred at room temperature for 3 h. After removal of the solvent under vacuum, 2 N HCl and ether were added to the residue. The organic phase was washed with water and dried over anhydrous $MgSO_4$. After concentration of the ether solution, vacuum distillation gave a colorless liquid of 4-(4-bromobutyl)styrene (26.0 g, 109 mmol, 55%, bp 92–94 °C/0.5 mmHg): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.85 (m, 4H, $CH_2CH_2CH_2CH_2Br$), 2.62 (t, 2H, J = 7 Hz, $ArCH_2$), 3.40 (t, 2H, J = 6 Hz, CH_2Br), 5.19 and 5.70 (2d, 2H, J = 11 and 18 Hz, $=CH_2$), dd, 1H, −CH=); 23 MHz ^{13}C NMR ($CDCl_3$) δ 29.8 (CH_2CH_2Br), 32.3 ($ArCH_2CH_2$), 33.6 (CH_2Br), 34.7 ($ArCH_2$), 113.1 ($=CH_2$), 126.3 (Ar, C2), 128.6 (Ar, C3), 135.5 (Ar, C1), 136.7 (−CH=), 141.6 (Ar, C4); IR (KBr, cm^{-1}) 826, 844, 906, 990, 1250, 1406, 1458, 1511, 1629.

4-(Bromomethyl)-1-methyl-2,6,7-trioxabicyclo[2.2.2]-octane. Under nitrogen atmosphere, a mixture of monobromopentaerythritol (15.1 g, 75.8 mmol), orthoacetic acid triethyl ester (12.4 g, 76.5 mmol), *p*-toluenesulfonic acid (0.05 g, 0.29 mmol), and toluene (20 mL) was heated at 90 °C for 7 h. The yielded ethanol was azeotropically removed. After cooling and concentration of the reaction mixture, solid distillation gave a white powder of 4-(bromomethyl)-1-methyl-2,6,7-trioxabicyclo-[2.2.2]octane (13.5 g, 60.4 mmol, 80%, mp 50.0–52.0 °C): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 3H, CH_3), 3.15 (s, 2H, $BrCH_2$), 4.02 (s, 6H, $C(CH_2O)_3C$).

4-(5-(4-Vinylphenyl)pentyl)-1-methyl-2,6,7-trioxabicyclo-[2.2.2]octane. (2) To a stirred suspension of magnesium ribbon (1.07 g, 44.0 mmol) in dry THF (3 mL) was added 4-(4-



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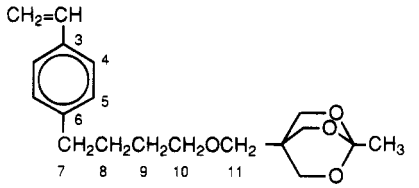
bromobutyl)styrene (8.51 g, 35.6 mmol) in 20 mL of dry THF dropwise at room temperature for 30 min. After complete consumption of 4-(4-bromobutyl)styrene, the reaction mixture was allowed to stand, and the supernatant was transferred to a dropping funnel. To a mixture of 4-(bromomethyl)-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane (7.00 g, 31.4 mmol), Li_2CuCl_4 (0.9 mmol),[21] and dry THF (11 mL) was added the THF solution of the Grignard reagent dropwise at room temperature, and then the solution was stirred for 3 h. After quenching with methanol, organic solvents were removed under vacuum. The solid residue was rinsed with hexane and diethyl ether, and the combined organic phase was dried over anhydrous Na_2SO_4. After concentration, the yellow residue was purified by flash column chromatography (Al_2O_3, hexane, and hexane/ethyl acetate = 10/1) to afford a colorless solid of **2** (1.19 g, 3.94 mmol, 13%, mp 33.1–35.5 °C). The monomer was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies: 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.16–1.70 (m, 8H, $ArCH_2CH_2CH_2CH_2CH_2$), 1.44 (s, 3H, CH_3), 2.57 (t, 2H, J = 7.5 Hz, $ArCH_2$), 3.89 (s, 6H, $C(CH_2O)_3C$), 5.18 and 5.69 (2d, 2H, J = 11 and 18 Hz, $=CH_2$), 6.70 (dd, 1H, −CH=), 7.05–7.37 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 23.0 (C10, CH_2), 23.5 (CH_3), 29.8 (C9, CH_2), 30.0 (C11, CH_2), 31.0 (C8, CH_2), 33.0 ($C(CH_2O)_3$), 35.6 (C7, $ArCH_2$), 71.3 ($C(CH_2O_3$), 108.3 (O_3C), 113.0 ($=CH_2$), 126.2 and 128.5 (Ar, C4 and Ar, C5), 135.4 (Ar, C3), 136.7 (−CH=), 142.0 (Ar, C6); IR (KBr, cm^{-1}) 855, 987, 1058, 1129, 1288, 1403, 1511, 1629.

4-(Hydroxymethyl)-1-methyl-2,6,7-trioxabicyclo[2.2.2]-octane.[18] Under nitrogen atmosphere, a mixture of pentaerythritol (17.7 g, 130 mmol), orthoacetic acid triethyl ester (21.5 g, 134 mmol), *p*-toluenesulfonic acid (0.16 g, 0.93 mmol), and toluene (17 mL) was heated at 90 °C for 9 h. The yielded ethanol was azeotropically removed. After cooling and concentration of the reaction mixture, solid distillation gave a white powder of 4-(hydroxymethyl)-1-methyl-2,6,7-trioxabicyclo-[2.2.2]octane (18.5 g, 115 mmol, 89%, mp 110.3–112.2 °C (lit.[18] 112 °C)): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 3H, CH_3), 1.93 (t, 1H, J = 3.4 Hz, OH), 3.46 (d, 2H, J = 3.4 Hz, $HOCH_2$), 4.03 (s, 6H, $C(CH_2O)_3C$).

4-[(4-(4-Vinylphenyl)butoxy)methyl]-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane. (3) To a mixture of 4-(hydroxymethyl)-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane (5.82 g, 36.4



3

mmol), potassium hydroxide (9.12 g, 161 mmol), and dimethyl sulfoxide (90 mL) was added 4-(4-bromobutyl)styrene (9.81 g, 41.1 mmol) in one portion, and the solution was stirred for 2 h at room temperature under nitrogen. The reaction mixture was diluted with water (800 mL) and then extracted with ether (200 mL × 4). The organic layer was washed with brine (200 mL) and water (200 mL) and dried over anhydrous Na_2SO_4. After concentration of the ether solution, the yellow residue was purified by flash column chromatography (Al_2O_3, hexane, and hexane/ethyl acetate = 10/1) to afford a colorless solid of **3** (7.50 g, 23.6 mmol, 65%). The resulting solid was thoroughly recrystallized from methanol and hexane to give a crystal of **3** (mp 57.0–58.2 °C). The purity of **3** was analyzed by HPLC and low molecular weight SEC measurements. The monomer was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies and elemental analysis: 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 3H, CH_3), 1.60 (m, 4H, $CH_2CH_2CH_2CH_2O$), 2.60 (t, 2H, J = 6.6 Hz, $ArCH_2$), 3.13 (s, 2H, OCH_2C), 3.34 (t, 2H, J = 6.3 Hz, CH_2CH_2O), 3.99 (s, 6H, $C(CH_2O)_3C$), 5.19 and 5.70 (2d, 2H, J = 11 and 18 Hz, $=CH_2$), 6.70 (dd, 1H, −CH=), 7.1–7.4 (m, 4H, aromatic); 23 MHz ^{13}C NMR ($CDCl_3$) δ 23.6 (CH_3), 27.9 (C8, CH_2), 29.0 (C9, CH_2), 35.1 ($C(CH_2O)_3$), 35.4 (C7, $ArCH_2$), 69.3 (CH_2CH_2O), 69.7 ($C(CH_2O)_3$), 71.8 (OCH_2C), 108.6 (O_3C), 113.0 ($=CH_2$), 126.3 and 128.6 (Ar, C4 and Ar, C5), 135.4 (Ar, C3), 136.8 (−CH=), 142.1 (Ar, C6); IR (KBr, cm^{-1}) 1635, 1402, 1392, 1295, 1213, 1134, 1108, 1063, 1050, 986. Anal. Calcd for **3**, $C_{19}H_{19}O_4$: C, 71.67; H, 8.23. Found: C, 71.37; H, 8.10.

Purification. After repeating recrystallizations, the purified monomers (**2** and **3**) were dried over P_2O_5 for 48 h at ambient temperature and sealed off in an apparatus equipped with a breakseal under high-vacuum conditions (10^{-6} mmHg). More effective purification was achieved by a vacuum distillation of **3** on a vacuum line after drying over CaH_2 at room temperature for 48 h in dry THF. The monomers were then diluted with THF in an all-glass ampule equipped with a breakseal, and the resulting monomer solutions (0.2 M in THF) were stored at −30 °C until ready to use for the polymerization.

Polymerization Procedures. All polymerizations were carried out at −78 °C in an all-glass apparatus equipped with breakseals with vigorous shaking under high-vacuum conditions, as previously reported.[2b] The polymerization was terminated with degassed methanol. The reaction mixture was poured into a large excess of methanol to precipitate a polymer. The resulting polymer was purified by reprecipitations in THF/MeOH and by freeze-drying from the benzene

solution. The polymer was then characterized by ^1H and ^{13}C NMR and IR spectroscopies. The following is the full list.

Poly(2): 90 MHz ^1H NMR ($CDCl_3$) δ 1.44 (s, 3H, CH_3), 0.8–2.5 (overlapping, 11H, CH_2CH and $ArCH_2CH_2CH_2CH_2CH_2$), 2.5 (broad, 2H, $ArCH_2$), 3.15 (s, 2H, OCH_2C), 3.89 (s, 6H, $C(CH_2O)_3C$), 6.2–7.3 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 23.1 (C10, CH_2), 23.5 (CH_3), 29.8 (C9, CH_2), 30.1 (C11, CH_2), 31.2 (C8, CH_2), 33.0 ($C(CH_2O)_3$), 35.5 (C7, $ArCH_2$), 40–43 (CH_2CH), 71.3 ($C(CH_2O)_3$), 108.3 (O_3C), 127.9 (overlapping, Ar, C4 and Ar, C5), 139 (Ar, C6), 143 (Ar, C3); IR (KBr, cm^{-1}) 868, 1008, 1058, 1127, 1298, 1353, 1401, 1511.

Poly(3): 90 MHz ^1H NMR ($CDCl_3$) δ 1.45 (s, 3H, CH_3), 1.0–2.5 (overlapping, 7H, CH_2CH and $CH_2CH_2CH_2CH_2O$), 2.5 (broad, 2H, $ArCH_2$), 3.15 (s, 2H, OCH_2C), 3.35 (broad, 2H, CH_2CH_2O), 4.00 (s, 6H, $C(CH_2O)_3C$), 6.2–7.2 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 23.6 (CH_3), 27.9 (C8, CH_2), 29.2 (C9, CH_2), 35.1 (overlapping, $C(CH_2O)_3$ and C7, $ArCH_2$), 40–45 (CH_2CH), 69.3 (CH_2CH_2O), 69.6 ($C(CH_2O)_3$), 71.7 (OCH_2C), 108.6 (O_3C), 127.8 (overlapping, Ar, C4 and Ar, C5), 139 (Ar, C6), 143 (Ar, C3); IR (KBr, cm^{-1}) 865, 990, 1055, 1127, 1210, 1297, 1389, 1511.

Block Copolymerization. In an all-glass apparatus in vacuo, the first-stage polymerization of **3** (1.72 mmol) was initiated with oligo(α-methylstyryl)lithium (0.0949 mmol) in THF at −78 °C. After 20 min, a small portion of the yielded living prepoly(**3**) (0.0128 mmol) was withdrawn to determine the characteristics of the first-stage polymer. To the residue of the polymerization system, styrene (6.84 mmol) in THF was added at −78 °C 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(**3**) and the poly(**3**-*b*-styrene) possessed predicted molecular weights and narrow molecular weight distributions, as shown in Table 2 (run 8). Similarly, the sequential copolymerization of styrene and **3** could quantitatively proceed to afford a well-defined block copolymer by the reversed addition of both comonomers.

Deprotection of Poly(3) (First Step). A mixture of poly(**3**) (0.20 g, 0.63 mmol based on monomer unit), 2 N HCl (0.1 mL), and THF (3.0 mL) was stirred at room temperature for 30 min. As the reaction proceeded, the precipitate was observed. A small amount of methanol was added to dissolve the precipitate and to keep the reaction system homogeneous. After 30 min, the reaction mixture was poured into a large excess of water to precipitate poly(**4**) (0.19 g, 0.58 mmol based on monomer unit, 92%). The polymer was characterized by ^1H and ^{13}C NMR spectroscopies.

Poly(4): 90 MHz ^1H NMR (CD_3OD) δ 1.2–2.2 (overlapping, 7H, CH_2CH and $CH_2CH_2CH_2CH_2O$), 2.05 (s, 3H, $COCH_3$), 2.5 (broad, 2H, $ArCH_2$), 3.3–3.8 (overlapping, 8H, $CH_2CH_2OCH_2C(CH_2OH)_2$), 4.15 (s, 2H, CH_2OAc), 6.2–7.2 (m, 4H, Ar); signals of the OH group were not observed due to the proton exchange in CD_3OD; ^1H NMR ($(CD_3)_2SO$) δ 1.1–2.2 (overlapping, 7H, CH_2CH and $CH_2CH_2CH_2CH_2O$), 1.95 (s, 3H, $COCH_3$), 2.5 (broad, 2H, $ArCH_2$), 3.2–4.3 (overlapping, 12H, $CH_2CH_2OCH_2C(CH_2OH)_2CH_2OAc$), 6.1–7.2 (m, 4H, Ar); 23 MHz ^{13}C NMR (CD_3OD) δ 20.9 (CH_3), 28.5 (C8, CH_2), 29.9 (C9, CH_2), 35.9 ($ArCH_2$), 45.4 ($CH_2C(CH_2OH)_2CH_2OAc$), 63.2 (CH_2OH), 64.3 (CH_2OAc), 71.4 and 72.4 ($CH_2CH_2OCH_2$), 128.4 (overlapping, Ar, C4 and Ar, C5), 140 (Ar, C6), 144 (Ar, C3) 172.4 (C=O); 23 MHz ^{13}C NMR ($(CD_3)_2SO$) δ 20.0 (CH_3), 26.9 (C8, CH_2), 28.4 (C9, CH_2), 34.2 ($ArCH_2$), 44.3 ($CH_2C(CH_2OH)_2CH_2OAc$), 60.7 (CH_2OH), 63.1 (CH_2OAc), 69.5 and 70.5 ($CH_2CH_2OCH_2$), 127.0 (overlapping, Ar, C4 and Ar, C5), 138.6 (Ar, C6), 142.2 (Ar, C3), 169.7 (C=O); the signals due to the CH_2CH group of the polymer backbone were not observed because of the overlapping of solvent signals; IR (KBr, cm^{-1}) 838, 1038, 1116, 1243, 1358, 1458, 1511, 1739 (C=O), 3200–3700 (OH).

Deprotection of Poly(3) (Second Step). A mixture of poly(**4**) (0.19 mmol, 0.58 mmol based on monomer unit), 10% NaOH solution (1 mL), and methanol (10 mL) was stirred at room temperature for 30 min. The reaction mixture was poured into a large excess of water to precipitate poly(**5**) (0.11 g, 0.41 mmol based on monomer unit, 71%). The polymer was characterized by ^1H and ^{13}C NMR spectroscopies.

Poly(5): 90 MHz ^1H NMR (CD_3OD) δ 1.1–2.1 (overlapping, 7H, CH_2CH and $CH_2CH_2CH_2CH_2O$), 2.5 (broad, 2H, $ArCH_2$), 3.1–3.8 (overlapping, 10H, $CH_2CH_2OCH_2C(CH_2OH)_3$), 6.2–7.2 (m, 4H, Ar); signals of the OH group were not observed due to the proton exchange in CD_3OD; ^1H NMR ($(CD_3)_2SO$) δ 1.1–1.9 (overlapping, 7H, CH_2CH and $CH_2CH_2CH_2CH_2O$), 2.5 (overlapping, 2H, $ArCH_2$), 3.1–4.0 (overlapping, 13H, $CH_2CH_2OCH_2C(CH_2OH)_3$), 6.1–7.1 (m, 4H, Ar); 23 MHz ^{13}C NMR (CD_3OD) δ 29.1 (C8, CH_2), 30.4 (C9, CH_2), 36.4 ($ArCH_2$), 41–44 (CH_2CH), 46.1 ($CH_2C(CH_2OH)_3$), 64.0 (CH_2OH), 72.3 and 72.8 ($CH_2CH_2OCH_2$), 129 (overlapping, Ar, C4 and Ar, C5), 141 (Ar, C6), 144 (Ar, C3); 23 MHz ^{13}C NMR ($(CD_3)_2SO$) δ 27.0 (C8, CH_2), 28.6 (C9, CH_2), 34.2 ($ArCH_2$), 45.0 ($CH_2C(CH_2OH)_3$), 61.7 (CH_2OH), 70.2 and 70.5 ($CH_2CH_2OCH_2$), 127.2 (overlapping, Ar, C4 and Ar, C5), 138.7 (Ar, C6), 142 (Ar, C3); the signals due to the CH_2CH group of the polymer main chain were not observed because of the overlapping of the solvent signals; IR (KBr, cm^{-1}) 1039, 1116, 1373, 1421, 1459, 1511, 3200–3700 (OH).

Acetylation of Hydroxyl Groups for Poly(5). To a solution of poly(**5**) (0.090 g, 0.31 mmol based on monomer unit) in dry pyridine (1.5 mL) was added acetic anhydride (3.0 mL) dropwise at 0 °C under nitrogen, and the reaction mixture was stirred at room temperature for 48 h. The reaction system was poured into a large excess of methanol to precipitate poly(**6**) (0.11 g, 0.26 mmol based on monomer unit, 84%). The polymer was characterized by ^1H and ^{13}C NMR and IR spectroscopies.

Poly(6): 90 MHz ^1H NMR ($CDCl_3$) δ 2.05 (s, 9H, $COCH_3$), 1.1–2.2 (overlapping, 7H, CH_2CH and $CH_2CH_2CH_2CH_2O$), 2.4 (broad, 2H, $ArCH_2$), 3.4 (broad, 4H, CH_2OCH_2C), 4.12 (s, 6H, $C(CH_2OAc)_3$), 6.1–7.1 (m, 4H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 20.6 ($COCH_3$), 27.7 (C8, CH_2), 29.4 (C9, CH_2), 35.2 ($ArCH_2$), 39–43 (overlapping, CH_2CH), 42.9 ($C(CH_2OAc)_3$), 63.1 ($C(CH_2OAc)_3$), 69.5 (CH_2CH_2O), 71.7 (OCH_2C), 127.8 (overlapping, Ar, C4 and Ar, C5), 139.1 (Ar, C6), 142.5 (Ar, C3) 170.3 ($COCH_3$); IR (KBr, cm^{-1}) 839, 906, 1040, 1116, 1231, 1366, 1468, 1511, 1742 (C=O).

Measurements. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^1H, 22.53 MHz ^{13}C) in $CDCl_3$, CD_3OD, or $(CD_3)_2SO$. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0) for ^1H NMR and to $CDCl_3$ (δ 77.1), CD_3OD (δ 49.0), and $(CD_3)_2SO$ (δ 39.5) for ^{13}C NMR as standards. 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.

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