Macromolecules **1994,** *27,* 35–39

Protection and Polymerization of Functional Monomers. 21. Anionic Living Polymerization of (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Methacrylate

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Received August 13, 1993; Revised Manuscript Received October 18, 1993[•]

ABSTRACT: The two hydroxy groups of 2,3-dihydroxypropyl methacrylate (**1**) were protected in the dioxolane form, (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (**2**). Anionic polymerization of **2** was investigated in THF at –78 °C with 1,1-diphenylhexyllithium, 1,1-diphenyl-3-methylpentyllithium, and α,ω-dilithiooligostyrene in the presence or absence of LiCl as well as with 1,4-disodio- and 1,4-dipotassio-1,1,4,4-tetraphenylbutanes. The polymerization of **2** proceeded to give poly(**2**) quantitatively in each case. Particularly, lithio initiators with LiCl afforded the poly(**2**)s of predictable molecular weights and of very narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ <1.1). Furthermore, the sequential polymerization of *tert*-butyl methacrylate with the anionic propagating end of poly(**2**) gave the block copolymer in quantitative efficiency. This indicates that anionic polymerization of **2** proceeds without transfer and termination reactions to yield a living polymer. Complete hydrolysis of the acetal protective group of poly(**2**) produced water-soluble poly(**1**). Addition of **2** to poly(styryl)lithium capped with 1,1-diphenylethylene in the presence of LiCl gave the block copolymers, which were hydrolyzed to result in poly(styrene-*b*-**1**) and poly(**1**-*b*-styrene-*b*-**1**) containing hydrophobic and hydrophilic segments.

Introduction

Recently, we have investigated the anionic living polymerizations of a series of monomers containing protected functional groups.[1] The protective group on each repeating unit of the resulting polymer is completely removed to regenerate the original function on the polymer chain having a predictable molecular weight and a very narrow molecular weight distribution. Thus, polystyrenes and polybutadienes with hydroxy, amino, mercapto, formyl, acetyl, and carboxy groups have been synthesized. In a similar manner, poly(2-hydroxyethyl methacrylate) (PHEMA) with a well-defined chain structure was produced through anionic living polymerization of 2-[(trimethylsilyl)oxy]ethyl methacrylate (HEMA–TMS) followed by deprotection of the trimethylsilyl group.[2] The sequential polymerization of HEMA–TMS with anionic living polystyrene produced the block copolymers, which were hydrolyzed under acidic condition to yield poly(HEMA-*b*-styrene-*b*-HEMA) with various block lengths. The block copolymer showed excellent nonthrombogenic activity compared with the related biomaterials, which was evaluated by *in vitro*, *ex vivo*, and *in vivo* experiments.[3–7] Furthermore, the surface structure of the block copolymer was characterized by XPS and static SIMS in comparison with that of a HEMA–styrene random copolymer.[8] Through the investigations on the polymer surface, the block copolymers containing hydrophilic and hydrophobic segments, like poly(HEMA-*b*-styrene-*b*-HEMA), were found to have characteristic surface structures and properties related to time, temperature, and environment. Although PHEMA is well-known as a hydrophilic polymer, PHEMA is not soluble in water and only absorbed water. Introduction of one more hydroxy group to the pendant of the methacrylate unit may result in a more hydrophilic polymer, and the amphiphilic block copolymer containing such hydrophilic segment may have different surface structure and properties. Thus, the objective of this research is to synthesize poly(2,3-dihydroxypropyl methacrylate) (poly(**1**)) having two hydroxy groups in the repeating unit, through anionic living polymerization of the protected monomer followed by deprotection of the resulting polymer.

Through our previous work on anionic living polymerizations of protected monomers, most of the hydroxy groups of 4-vinylphenol,[9] 2-(4-vinylphenyl)ethanol,[10] 3-(hydroxymethyl)styrene,[11] and HEMA[2] were masked with trialkylsilyl groups. As an alternative, acetals are routinely used as protecting groups for hydroxy functions in synthetic chemistry.[12] Schulz *et al.* described that organolithium reagents containing acetal groups initiated the polymerization of butadiene to afford the anionic living polymer.[13] Protection of the carbonyl group can also be achieved by an acetal linkage as reported in the case of the anionic living polymerization of 3-formylstyrene.[14] As shown in many synthetic routes, acetals are stable to highly reactive basic and nucleophilic reagents but are readily cleaved under mild acidic conditions. Likewise, the two hydroxy groups of **1** may be suitably protected with a dioxolane linkage in the form of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (**2**) against the anionic initiator and the propagating carbanion. As shown in Scheme I, the anionic polymerization of **2** is expected to proceed without transfer and termination reactions. Furthermore, the resulting poly(**2**) may be deprotected quantitatively to yield poly(**1**) with well-defined chain structures.

Experimental Section

Materials. Tetrahydrofuran (THF) was refluxed over a Na wire, distilled over LiAlH$_4$, and again distilled from the sodium naphthalenide solution on a vacuum line. 1,1-Diphenylethylene (DPE) was dried and distilled over CaH$_2$ and finally distilled from the 1,1-diphenylhexyllithium solution under reduced pressure. Commercially available *sec*-butyllithium (*sec*-BuLi) and *n*-butyllithium (*n*-BuLi) were used without further purification. Anionic initiators used here were obtained prior to the polymerization as follows: 1,1-diphenyl-3-methylpentyllithium and 1,1-diphenylhexyllithium were prepared in THF by the reactions of

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[•] Abstract published in *Advance ACS Abstracts,* December 1, 1993.

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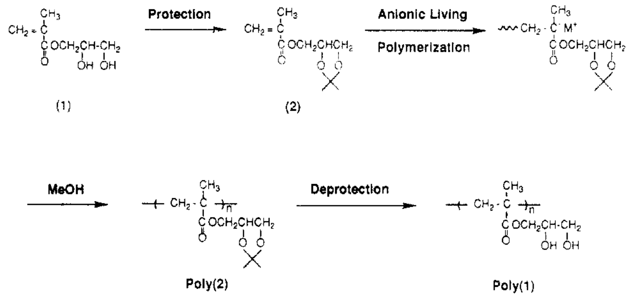
Scheme 1



sec-BuLi with an excess of DPE at −78 °C for 15 min and *n*-BuLi with an excess of DPE at room temperature for 20 s and then at −78 °C for 15 min, respectively. Metal naphthalenides were prepared by contact of a slight excess of naphthalene with the corresponding alkaline metals in THF. 1,4-Disodio- and 1,4-dipotassio-1,1,4,4-tetraphenylbutanes were prepared from the corresponding metal naphthalenides and an excess of DPE in THF at −78 °C for 15 min. The concentrations of the initiators were determined by colorimetric titration using standardized 1-octanol in THF in a sealed tube with break-seals. LiCl was dried under high vacuum (10^{-6} mmHg) for 48 h with baking for every 1 h. *tert*-Butyl methacrylate (BMA) and styrene were washed with 5% aqueous NaOH and water, dried over $MgSO_4$, again dried over CaH_2 for 48 h, and distilled over CaH_2 under reduced pressure. Styrene was finally distilled on a vacuum line from the benzylmagnesium chloride solution. BMA was finally distilled over trioctylaluminum on a vacuum line and diluted to a 0.6–0.8 M solution with THF for the polymerization by a vacuum system according to the previously reported method.[15,16]

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl Methacrylate (2). 2 was prepared from isopropylidene glycerol and methacryloyl chloride according to the reported method.[17] To the mixture of isopropylidene glycerol[18] (21.2 g, 0.16 mol) and triethylamine (16.3 g, 0.16 mol) in benzene (400 mL) was added dropwise methacryloyl chloride (12.5 g, 0.12 mol) in benzene (25 mL) with stirring at 0 °C. The reaction mixture was stirred at room temperature overnight under a nitrogen atmosphere. The triethylamine hydrochloride precipitated was removed from the solution by filtration, and the solution was washed twice with distilled water and dried with anhydrous sodium carbonate. After filtration, benzene was evaporated under reduced pressure to yield a pale orange liquid. The product was purified by fractional distillation at 53–55 °C (1.5 mmHg) [lit.[17] 57–60 °C (2.0 mmHg)] in the presence of methylene blue as an inhibitor to give 12.0 g (0.06 mol, 50%) of 2 as a colorless liquid: ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.10 (s, 1H, HC=C, trans), 5.59 (s, 1H, HC=C, cis), 3.7–4.5 (m, 5H, CH_2CHCH_2), 1.96 (s, 3H, $=CCH_3$), 1.43, 1.38 (two s, 6H, $C(CH_3)_2$); ^{13}C NMR (22.5 Hz, $CDCl_3$) δ 166.9 (C=O), 135.9 (=C), 125.7 ($CH_2=$), 108.6 (OCO), 73.6 ($COOCH_2CH$), 66.3 ($COOCH_2CHCH_2$), 64.6 ($COOCH_2$), 26.6, 25.3 ($C(CH_3)_2$), 18.1 ($=CCH_3$); IR (neat) 1730 (C=O), 1370 cm^{-1} ($C(CH_3)_2$). In the case of the polymerization under high-vacuum conditions, 2 was finally purified in a manner similar to that of BMA. For the polymerization under an argon overpressure, 2 in THF was purified by shaking with active alumina, which have an Al–C_2H_5 bond on the surface via the reaction with triethylaluminum.

Polymerization Procedure. Polymerizations were carried out at −78 °C with stirring under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with break-seals. In some cases, polymerizations were also carried out in a bottle under an argon overpressure. The desired charge of monomer in THF was added to a THF solution of initiator with vigorous shaking. After the polymerization solution was allowed to stand for several hours at −78 °C, the reaction mixture was quenched with methanol and was concentrated under reduced pressure. The residue was dissolved in benzene and washed with distilled water. After evaporation, the residual polymer was again dissolved in a small amount of THF and poured into hexane to precipitate the polymer. The polymer was purified by reprecipitation from a THF solution into hexane and freeze-dried from benzene: ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.6–4.6 (m, 5H, CH_2CHCH_2), 1.5–2.4 (br s, 2H, CH_2), 1.43, 1.38 (two s, 6H, $C(CH_3)_2$), 0.6–1.4 (br s, 3H, α-CH_3); ^{13}C NMR (22.5 Hz, $CDCl_3$) δ 177.2, 176.8, 176.0 (C=O), 109.7 (OCO), 72.9 ($COOCH_2CH$), 66.4 ($COOCH_2CHCH_2$), 64.5 ($COOCH_2$), 54.7, 54.4 (CH_2), 45.0, 44.8 (–C–), 26.8, 25.3 ($C(CH_3)_2$), 18.9, 17.0 (α-CH_3); IR (KBr) 1730 (C=O), 1370 cm^{-1} ($C(CH_3)_2$). Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05; N, 0.00. Found: C, 59.40; H, 8.15; N, 0.00.

Similarly, block copolymerization was carried out by the sequential addition of monomers to the polymerization system. Poly(2-*b*-BMA) obtained was purified in a manner similar to that of poly(2). THF solutions of poly(styrene-*b*-2) and poly(2-*b*-styrene-*b*-2) were poured into methanol to precipitate the polymer, which was freeze-dried from benzene.

Deprotection of Poly(2) and the Block Copolymers. To the solution of poly(2) (0.30 g) in 1,4-dioxane (9 mL) was added aqueous 1 N HCl (3 mL) dropwise at 0 °C, and the solution was stirred at room temperature for 24 h. The solution became turbid on addition of aqueous HCl and then gradually cleared as the reaction progressed. The solution was poured into hexane–EtOH (1:1) to precipitate the polymer, which was again reprecipitated from THF–MeOH to hexane–EtOH (1:1) and freeze-dried from 1,4-dioxane containing a small amount of MeOH, to give a white solid. The yield of polymer was quantitative. The polymer was identified as poly(1) by ^{1}H and ^{13}C NMR and IR spectra: ^{1}H NMR (90 MHz, CD_3OD) δ 3.4–4.6 (br m, 5H, CH_2CHCH_2), 1.5–2.4 (br s, 2H, CH_2), 0.5–1.4 (br s, 3H, α-CH_3); ^{13}C NMR (22.5 Hz, CD_3OD) δ 179.5, 179.2, 178.4 (C=O), 70.8, 67.4, 64.2 (CH_2CHCH_2), 49.3, 46.3 (–C–), 19.8, 17.7 (CCH_3); IR (KBr) 1717 (C=O), 3000–3800 cm^{-1} (OH). Anal. Calcd for $C_7H_{12}O_4\cdot{}^1/_5H_2O$: C, 51.34; H, 7.63; N, 0.00. Found: C, 51.67; H, 7.48; N, 0.00.

Deprotection of poly(2-*b*-styrene-*b*-2) and poly(styrene-*b*-2) and the workup procedure of the resulting polymers were performed in a manner similar to that for poly(2).

Measurements. Infrared (IR) spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q in ppm downfield relative to $(CH_3)_4Si$ (δ 0) and $\mathit{CH_3}OH$ (δ 3.35) for ^{1}H NMR and relative to $CDCl_3$ (δ 77.1) and CD_3OD (δ 49.0) for ^{13}C NMR. Size-exclusion chromatograms (SEC) were obtained at 40 °C with a Tosoh HLC-8020 with three polystyrene gel columns (Tosoh G5000H × 1, G4000H × 1, and G3000H × 1) using THF as an eluent at a flow rate of 1.0 mL/min. Vapor-pressure osmometry (VPO) measurement was made in benzene with a Corona 117.

Results and Discussion

Previously, Beinert, Hild, and Rempp briefly reported anionic polymerization of 2 with 1,4-disodio-1,1,4,4-tetraphenylbutane as an initiator in THF at −60 °C and deprotection of the resulting poly(2) with aqueous HCl to yield poly(1).[19] However, the molecular weights and the molecular weight distributions of the polymers produced were not described in detail. In this paper, we have substantiated the anionic living polymerization of 2 in the presence of LiCl and the block copolymerizations of 2 with *tert*-butyl methacrylate (BMA) and styrene.

Addition of the protected monomer, 2, to the THF solution of 1,1-diphenylhexyllithium was followed by an instantaneous disappearance of the characteristic red color, indicating a rapid initiation reaction. The monomer was consumed in a few minutes at −78 °C to yield the polymer quantitatively. IR and ^{1}H and ^{13}C NMR of the resulting polymer gave evidences for the expected structure of the vinyl polymer of 2 with the acetal function intact during the polymerization and workup processes. The results of the polymerization are listed in Tables 1 and 2. The molecular weights of the polymers generated with 1,1-diphenylhexyllithium, α,ω-dilithiooligostyrene capped with DPE, and 1,4-disodio- and 1,4-dipotassio-1,1,4,4-tetraphenylbutanes agree with those based on the ratio of monomer to initiator, although the molecular weight distributions are somewhat broader. The experiment of Rempp *et al.*, the anionic polymerization of 2 initiated with 1,4-disodio-1,1,4,4-tetraphenylbutane in THF at −60 °C, was traced

Table 1. Anionic Polymerization of 2 with 1,1-Diphenylhexyllithium–LiCl in THF at –78 °C for 0.5–1 h[a]

2, mmol	n-BuLi, mmol	1,1-diphenylethylene, mmol	LiCl, mmol	$10^{-3}\bar{M}_n$		$\bar{M}_w/\bar{M}_n$[c]
				calcd	obsd[b]	
4.55[d]	0.0986	0.170		9.5	9.9	1.23
3.55[d]	0.0925	0.157	0.264	7.9	8.1	1.05
4.76[d,f]	0.0974	0.172	0.225	10	10	1.05
4.36[d]	0.0509	0.0925	0.167	17	18	1.07
5.32[d,f]	0.0414	0.0878	0.158	26	26	1.03
2.69[d]	0.0762[g]	0.122	0.227	7.2	7.2	1.04
7.64[e]	0.451	0.920	1.93	3.6	3.9	1.08
7.47[e]	0.180	0.367	0.622	8.5	8.6	1.08

[a] Yields of polymers were quantitative in all cases. [b] $\bar{M}_n$(obsd) was obtained by VPO. [c] $\bar{M}_w/\bar{M}_n$ was determined from the SEC curve, using standardized poly(MMA)s for calibration. [d] Polymerization was carried out under a high-vacuum condition. [e] Polymerization was carried out under an argon overpressure. [f] Polymerization time was prolonged to 12 h. [g] *sec*-BuLi was used in place of *n*-BuLi.

Table 2. Anionic Polymerization of 2 with Difunctional Initiators in THF at –78 °C for 0.5–12 h[a]

2, mmol	initiator		DPE,[b] mmol	LiCl, mmol	$10^{-3}\bar{M}_n$		$\bar{M}_w/\bar{M}_n$[d]
	countercation	mmol			calcd	obsd[c]	
5.94	K^{+}[e]	0.120	0.175		20	23	1.21
4.57	Na^{+}[e]	0.100	0.158		19	18	1.32
2.90	Li^{+}[f]	0.0762	0.248		19	20	1.44
2.52	Li^{+}[f]	0.0634	0.149	0.270	19	18	1.09

[a] Yields of polymers were quantitative in all cases. [b] 1,1-Diphenylethylene. [c] $\bar{M}_n$(obsd) was obtained by VPO. [d] $\bar{M}_w/\bar{M}_n$ was determined from the SEC curve. [e] Metal naphthalenides used as initiator. [f] α,ω-Dilithiooligostyrene oligomer used as initiator.

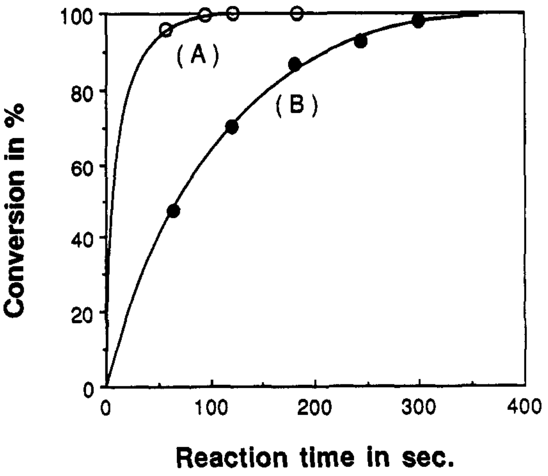


Figure 1. Time–conversion curves for the polymerization of 2 by 1,1-diphenylhexyllithium in THF at –78 °C under an argon overpressure in the absence (A) and in the presence (B) of LiCl: (A) $[1]_0$ = 0.006 80 M, $[2]_0$ = 0.740 M, $[LiCl]_0$ = 0; (B) $[1]_0$ = 0.0118 M, $[2]_0$ = 0.740 M, $[LiCl]_0$ = 0.040 6 M.

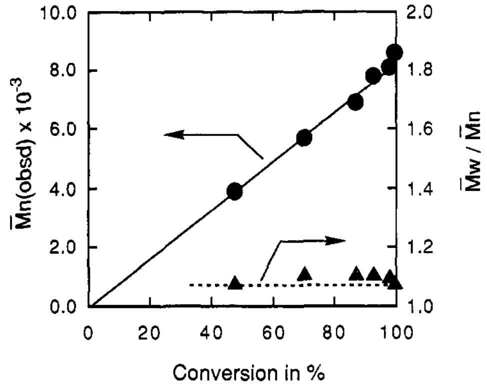


Figure 2. Relationship between molecular weight and molecular weight distribution of poly(2) against conversion. The conditions of the polymerization are shown in Figure 1B. The solid line indicates the theoretical molecular weight.

here under similar conditions to give poly(2) in quantitative yield.

Teyssié and his co-workers found a striking effect of LiCl on the anionic polymerizations of *tert*-butyl acrylate[20] and MMA[21] to yield the polymers of narrow molecular weight distributions. Recently, we have also reported the anionic living polymer of 3-(trialkoxysilyl)propyl methacrylates in the presence of LiCl.[16] In expectation of such an effect of LiCl, the anionic polymerization of 2 was also examined with LiCl. As can be seen in Tables 1 and 2, the poly(2)s obtained with 1,1-diphenylhexyllithium, 1,1-diphenyl-3-methylpentyllithium, and α,ω-dilithiooligostyrene capped with DPE in the presence of LiCl have very narrow molecular weight distributions compared with those produced in the absence of LiCl. The observed molecular weights of the poly(2)s are very close to those calculated. In addition, prolonged reaction time (12 h) did not affect the molecular weight and molecular weight distribution of the polymer obtained. This indicates that the carbanion at the propagating end did not attack the protective group even over a long reaction time. As shown in Table 1, the molecular weight and molecular weight distribution were precisely controlled under an argon overpressure as well as under a high-vacuum condition.

The time course of the polymerization of 2 was followed under an argon overpressure in THF at –78 °C in the presence and absence of LiCl using 1,1-diphenylhexyllithium as an initiator. As can be seen in Figure 1, the polymerization rate of 2 was extremely high without LiCl and resulted in complete reaction within 2 min. However, the addition of LiCl([LiCl]/[I] = 3.4) to this system lowered the polymerization rate significantly and completion of the reaction required at least 15 min. The rate constant of the polymerization was estimated to be almost one-tenth of that without LiCl. Such retardations of the polymerization rates of (meth)acrylates were reported by Kunkel and Müller[22] and Teyssié *et al.*[21] Furthermore, Teyssié suggested that undesirable side reactions, like backbiting, were eliminated through steric hindrance around the lithium countercation complexed with LiCl. Both effects of LiCl may contribute to the formation of poly(2) of very narrow molecular weight distribution.

Figure 2 shows the relationship between the molecular weight and molecular weight distribution of poly(2) against % conversion in the presence of LiCl under the condition described in Figure 1B. The molecular weight increased linearly with conversion of 2 in accordance with the calculated value based on the consumed monomer to initiator ratio. The molecular weight distribution was very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) throughout the polymerization. In addition to the data shown in Tables 1 and 2, these results indicate that the polymerization with lithium initiators in the presence of LiCl proceeds without termination and transfer reactions to give the living poly(2).

Block Copolymerization. To confirm the persistency of activity at the propagating chain end of poly(2), block copolymerization of 2 with BMA was carried out. The reaction mixture of 2 with 1,1-diphenyl-3-methylpentyllithium and LiCl in THF was kept at –78 °C for 30 min. An aliquot was withdrawn from the solution for the analysis of the homopolymer. To the remaining mixture was added BMA for block copolymerization at –78 °C for 6 h. Both homopolymers and block copolymers were quantitatively produced. The results are summarized in Table 3. Good agreements were obtained between the observed and

Table 3. Block Copolymerization of 2 with *tert*-Butyl Methacrylate and Styrene[a]

block sequence	A monomer	B monomer	block copolymer (homopolymer)[b] $10^{-3}\bar{M}_n$ (calcd)	$10^{-3}\bar{M}_n$ (obsd)	$\bar{M}_w/\bar{M}_n$[d]
A–B[e]	2	BMA[h]	20 (2.7)	23 (2.3)	1.03 (1.11)
A–B[f]	styrene	2	18 (8.1)	18 (8.4)	1.06 (1.04)
B–A–B[g]	styrene	2	27 (12)	26 (13)	1.08 (1.06)

[a] Block copolymerizations were carried out in the presence of LiCl in THF at −78 °C. Yields of polymers were quantitative in all cases. [b] Homopolymers were obtained in the first-stage polymerization. [c] $\bar{M}_n$(obsd) was obtained by SEC and VPO and ^{1}H NMR. [d] $\bar{M}_w/\bar{M}_n$ was determined from the SEC curve. [e] 1,1-Diphenyl-3-methylpentyllithium was used as an initiator. [f] Living polystyrene initiated with *n*-BuLi was capped with DPE before addition of **2**. [g] Living polystyrene initiated with Li-Naph was capped with DPE before addition of **2**. [h] *tert*-Butyl methacrylate.

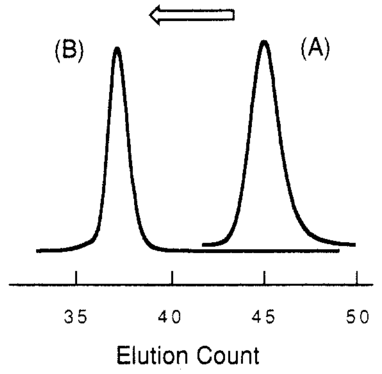


Figure 3. GPC curves for poly(**2**) produced in the first polymerization, $\bar{M}_n$(obsd) = 2300, $\bar{M}_w/\bar{M}_n$ = 1.11 (A), and poly(**2**-*b*-BMA) produced in block copolymerization, $\bar{M}_n$(obsd) = 23 000, $\bar{M}_w/\bar{M}_n$ = 1.03 (B).

calculated molecular weights of the homopolymers and block polymers. Furthermore, the resulting poly(**2**) and poly(**2**-*b*-BMA) possessed fairly narrow molecular weight distributions. As shown in Figure 3, the GPC curve of the homopolymer clearly shifted toward that of the block copolymer in the higher molecular weight region without any peak at the elution count of the homopolymer. This indicates that the propagating chain end of poly(**2**) is stable under the condition and able to initiate further polymerization of BMA with quantitative efficiency. Thus, the living nature of anionically initiated poly(**2**) is substantiated.

Other types of block copolymers, poly(styrene-*b*-**2**) and poly(**2**-*b*-styrene-*b*-**2**), were synthesized to derive new block copolymers containing hydrophilic and hydrophobic segments by hydrolysis of the acetal linkage on the poly(**2**) chain. Mono- and difunctional DPE-capped living polystyrenes were prepared by *n*-butyllithium and lithium naphthalenide, respectively, followed by the addition of DPE. Anionic polymerizations of **2** were initiated with the living polystyrenes in the presence of LiCl at −78 °C in THF to give the block copolymers in quantitative yields. The results are summarized in Table 3. The composition of each segment determined by ^{1}H NMR is almost equal to that of the fed monomers. The molecular weights of the block copolymers, which are estimated from those of the starting polystyrenes and compositions of the segments, are very close to the calculated ones. The block copolymers possess single SEC peaks and fairly narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.06–1.08). Further propagation of **2** from the living polystyrene is also confirmed by a complete shift of the SEC profile of the starting polystyrene to higher molecular weight. All of these results clearly indicate that the DPE-capped living polystyrene initiates the polymerization of **2** in the presence of LiCl to afford the block copolymer with as-designed chain structure. Transformation of the block copolymer to an amphiphilic one by deprotection will be mentioned below.

Removal of the Acetal Protecting Group in Poly(2) and the Block Copolymers. The 1,3-dioxolane ring in poly(**2**) was readily cleaved to regenerate the diol function by treating the polymer with 1 N HCl in 1,4-dioxane at room temperature for 24 h. The deprotected poly(**1**) was purified by reprecipitation from THF–methanol to hexane–EtOH (1:1) to give a white solid. As mentioned in the Experimental Section, the result of elemental analysis of the poly(**1**) was consistent with the calculated value including $^1/_5$ water molecule per repeating unit, which showed the hydrophilicity of the polymer. In the IR spectrum of poly(**1**), a very strong OH stretching band due to the diol function appeared at 3000–3800 cm^{-1}, where no absorption was observed for poly(**2**). The deformation band due to the geminal methyl group of the dioxolane ring at 1370 cm^{-1} diminished after deprotection. Characteristic C=O stretching absorptions appeared at 1730 and 1717 cm^{-1} for poly(**2**) and poly(**1**), respectively, suggesting that hydrogen bonding between carbonyl and diol functions in the poly(**1**) chain caused a decrease in the carbonyl frequency. In the NMR spectra of poly(**1**), methyl proton signals of the 1,3-dioxolane ring at 1.38 and 1.43 ppm and carbon signals of the dioxolane ring at 109.7 ppm (OCO) and at 26.8 and 25.3 ppm ($C(CH_3)_2$) thoroughly disappeared after deprotection of poly(**2**). Thus, within the experimental limits, these analytical data reveal that the complete removal of the protecting group from poly(**2**) was achieved.

The poly(**1**) obtained here was soluble in *N,N*-dimethylformamide, pyridine, methanol, and water and insoluble in hexane, cyclohexane, benzene, toluene, carbon tetrachloride, chloroform, dichloromethane, diethyl ether, 1,4-dioxane, THF, ethyl acetate, acetone, methyl ethyl ketone, and ethanol. In contrast, PHEMA is insoluble in water and soluble in ethanol, which indicates that two hydroxy groups on the repeating unit of poly(**1**) enhanced the hydrophilicity significantly. For SEC measurement, benzoylation of poly(**1**) was performed by the reaction of benzoic anhydride in pyridine. A very narrow and unimodal molecular weight distribution was observed in the SEC of benzoylated poly(**1**), indicating that no main-chain cleavage and cross-linking occurred during the deprotecting procedure. Thus, we were successful in synthesizing water-soluble, linear poly(**1**)s of predicted molecular weights and of narrow molecular weight distributions.

Deprotection of the poly(**2**) segments in poly(styrene-*b*-**2**) and poly(**2**-*b*-styrene-*b*-**2**) was also successfully achieved in a manner similar to that described above to afford new amphiphilic block polymers, poly(styrene-*b*-**1**) and poly(**1**-*b*-styrene-*b*-**1**), which can be compared to the block copolymers of styrene and HEMA. The solubility of the block copolymer depends upon the segment composition; for the typical case, $(\text{styrene})_{81}$-*b*-$(\mathbf{1})_{49}$ was soluble in THF, 1,4-dioxane, *N,N*-dimethylformamide, and pyridine and insoluble in hexane, benzene, dichloromethane, chloroform, carbon tetrachloride, ethyl acetate, acetone, methanol, ethanol, and water. Microphase-separated structure in a solid, surface structure, and biocompatibility of the block copolymers of styrene and **1** are very interesting research subjects compared with those of styrene–HEMA block copolymers, which will be described in detail elsewhere.

References and Notes

(1) For a review, see: Nakahama, S.; Hirao, A. *Prog. Polym. Sci.* **1990**, *15*, 299.

(2) Hirao, A.; Kato, H.; Yamaguchi, K.; Nakahama, S. *Macromolecules* **1986**, *19*, 1294.

(3) Okano, T.; Aoyagi, T.; Kataoka, K.; Abe, K.; Sakurai, Y. *J. Biomed. Mater. Res.* **1986**, *20*, 919.

(4) Nojiri, C.; Okano, T.; Park, K. D.; Kim, S. W. *ASAIO Trans.* **1988**, *34*, 386.

(5) Nojiri, C.; Okano, T.; Grainger, D.; Park, K. D.; Nakahama, S.; Suzuki, K.; Kim, S. W. *ASAIO Trans.* **1987**, *33*, 596.

(6) Nojiri, C.; Okano, T.; Jacobs, H. A.; Park, K. D.; Mohammad, S. F.; Olsen, D. B.; Kim, S. W. *J. Biomed. Mater. Res.* **1990**, *24*, 1151.

(7) Nojiri, C.; Okano, T.; Koyanagi, H.; Nakahama, S.; Park, K. D.; Kim, S. W. *J. Biomater. Sci. Polym. Ed.* **1992**, *4*, 75.

(8) Castner, D. G.; Ratner, B. D.; Grainger, D. W.; Kim, S. W.; Okano, T.; Suzuki, K.; Briggs, D.; Nakahama, S. *J. Biomater. Sci. Polym. Ed.* **1992**, *3*, 463.

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

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

(11) Hirao, A.; Kitamura, K.; Takenaka, K.; Nakahama, S. *Macromolecules* **1993**, *26*, 4995.

(12) Green, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley-Interscience: New York, 1991; p 10.

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

(14) Ishizone, T.; Kato, R.; Ishino, Y.; Hirao, A.; Nakahama, S. *Macromolecules* **1991**, *24*, 1449.

(15) Allen, R. D.; Long, T. E.; McGrath, J. E. *Polym. Bull.* **1986**, *15*, 127.

(16) Ozaki, H.; Hirao, A.; Nakahama, S. *Macromolecules* **1992**, *25*, 1391.

(17) Oguchi, K.; Sanui, K.; Ogata, N.; Takahashi, Y.; Nakada, T. *Polym. Eng. Sci.* **1990**, *30*, 449.

(18) *Organic Syntheses*; John Wiley & Sons: New York, 1955; Collect. Vol. III, p 502.

(19) Beinert, G.; Hild, G.; Rempp, P. *Makromol. Chem.* **1974**, *175*, 2069.

(20) Fayt, R.; Forte, R.; Jacobs, C.; Jérôme, R.; Ouhadi, T.; Teyssié, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442.

(21) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1990**, *23*, 2618.

(22) Kunkel, D.; Müller, A. H. E. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 315.