Synthesis of Water-Soluble Polymethacrylates by Living Anionic Polymerization of Trialkylsilyl-Protected Oligo(ethylene glycol) Methacrylates

Takashi Ishizone,* Seok Han, Syunsuke Okuyama, and Seiichi Nakahama

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-8552 Japan

Received August 5, 2002

ABSTRACT: 2-[2-[(*tert*-Butyldimethylsilyl)oxy]ethoxy]ethyl methacrylate (**2**) and 2-[2-[2-[(*tert*-butyldimethylsilyl)oxy]ethoxy]ethoxy]ethyl methacrylate (**3**) were polymerized anionically in THF at −78 °C for 2−24 h. The anionic initiator systems included 1,1-diphenyl-3-methylpentyllithium/lithium chloride and diphenylmethylpotassium/diethylzinc. The polymerization of novel *tert*-butyldimethylsilyl-protected oligo(ethylene glycol) methacrylates, **2** and **3**, proceeded quantitatively in each case. The resulting polymers possessed the predicted molecular weights based on the molar ratios of monomers to initiators, and narrow molecular weight distributions (M_w/M_n < 1.1). The stability of the propagating carbanion of poly(**2**) and poly(**3**) was ascertained by the quantitative efficiencies of the sequential block copolymerizations using *tert*-butyl methacrylate (tBMA). Well-defined block copolymers, poly(**2**)-*block*-poly(tBMA) and poly(**3**)-*block*-poly(tBMA), were obtained. The trialkylsilyl protecting groups of poly(**2**) and poly(**3**) were quantitatively hydrolyzed using 2 N HCl in aqueous THF at 0 °C for 2 h to give tailored poly[di(ethylene glycol) methacrylate] and poly[tri(ethylene glycol) methacrylate], respectively. Both polymethacrylates obtained after deprotection were readily soluble in water due to the high polarity of the hydrophilic oligo(ethylene glycol) pendant units with terminal OH functionality.

Introduction

Although the living anionic polymerization of hydrocarbons such as styrenes and 1,3-dienes is the most established synthetic tool for producing homopolymers and block copolymers with well-defined chain structures,[1] it is difficult to polymerize directly functional monomers containing acidic and/or electrophilic functional groups under anionic conditions. Since the reactive functional groups readily react with anionic initiators and propagating carbanions, if produced, the functional groups in the monomers must be protected prior to anionic polymerization. We have succeeded in the living anionic polymerizations of a series of monomers containing suitable protected functional groups,[2] to produce well-defined polystyrenes and polybutadienes with a variety of functional groups such as hydroxy, amino, mercapto, formyl, acetyl, carboxyl, and ethynyl groups after complete removal of the protecting groups.

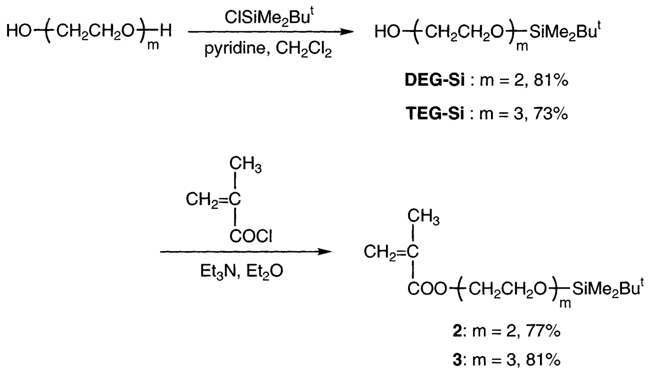
This strategy is also very effective for the tailored synthesis of functional polymethacrylates containing hydroxy groups in each monomer unit. Poly(2-hydroxyethyl methacrylate), poly(HEMA), with predicted molecular weight and narrow molecular weight distribution (MWD) can be synthesized via the anionic living polymerizations of 2-[(trimethylsilyl)oxy]ethyl methacrylate,[3,4] 2-[(*tert*-butyldimethylsilyl)oxy]ethyl methacrylate (**1**),[4] and 2-[(methoxymethyl)oxy]ethyl methacrylate,[4] followed by the successive deprotections. Poly(HEMA), the ester of ethylene glycol, is a hydrophilic polymer that has attracted a great deal of attention over the years, particularly for biomedical applications such as contact lenses, hydrogels, and hemodialysis membranes. The amphiphilic triblock copolymer, poly(HEMA)-*block*-polystyrene-*block*-poly(HEMA), has excellent nonthrombogenic activity compared to other polymers, probably due to its microphase separated surface.[5,6] However, the hydrophilic poly(HEMA) is not soluble in water, whereas it is extremely hygroscopic.

Poly(2,3-dihydroxypropyl methacrylate), poly(DIMA), which has two hydroxy groups in each monomer unit, is more hydrophilic and readily soluble in water.[7] Well-defined poly(DIMA), the ester of glycerine, has been synthesized via either the living anionic polymerization of acetal-protected (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate[7] or by chemical modification of anionically synthesized poly(allyl methacrylate).[8] Amphiphilic block copolymers containing water-soluble poly(DIMA) segments also exhibit interesting surface structures and properties.[9] Thus, introduction of one more hydroxy group to the pendant ester moiety of each repeat unit solubilizes the polymethacrylate in water.

The present paper reports another molecular design directed to water-soluble polymethacrylates, by introducing hydrophilic oligo(ethylene glycol) units in the side chain. The candidates are the poly(methacrylic acid) esters of di(ethylene glycol) and tri(ethylene glycol), poly(DEGMA), and poly(TEGMA), respectively. Although the cross-linked hydrogels of these polymers have been prepared via free-radical polymerization in the presence of cross-linkable dimethacrylates,[10,11] examples of linear soluble polymers are extremely limited. In this study, the ω-hydroxy groups in the side chain of monomers were masked with bulky and stable *tert*-butyldimethylsilyl groups[12] prior to polymerization, as shown in Scheme 1. We herein attempt the anionic polymerization of novel protected monomers, 2-[2-[(*tert*-butyldimethylsilyl)oxy]ethoxy]ethyl methacrylate (**2**) and 2-[2-[2-[(*tert*-butyldimethylsilyl)oxy]ethoxy]ethoxy]ethyl methacrylate (**3**), followed by deprotection of the resulting polymers to synthesize well-defined poly[oligo(ethylene glycol) methacrylate]s showing water-solubility.

10.1021/ma021257f CCC: $25.00

Scheme 1



Results and Discussion

Synthesis of 2 and 3. In this study, we have employed the stable *tert*-butyldimethylsilyl group as a protecting group for OH functions[12] in di(ethylene glycol) methacrylate (DEGMA) and tri(ethylene glycol) methacrylate (TEGMA), since it tolerates the monomer purification, including extraction and column chromatography, and the direct polymer characterizations. The trimethylsilyl protecting group is rather unstable and is gradually cleaved from the isolated polymer even under the neutral conditions. The *tert*-butyldimethylsilyl ether can be removed under both acidic conditions and under neutral conditions using tetrabutylammonium fluoride (Bu_4NF),[12] whereas relatively severe acidic conditions are necessary to cleave the corresponding methoxymethyl ether.

Monomers **2** and **3** were synthesized by reaction of methacryloyl chloride with either *tert*-butyldimethylsilyl ether of di(ethylene glycol) or the corresponding silyl ether of tri(ethylene glycol) in the presence of triethylamine in diethyl ether, as shown in Scheme 1. A considerable amount of either di(ethylene glycol) dimethacrylate or tri(ethylene glycol) dimethacrylate was formed as byproducts. These difunctional vinyl compounds act as cross-linking reagents in the polymerizations of **2** and **3**,[10,11] if they are not completely removed. Therefore, we have thoroughly purified the protected monomers by repeating column chromatography and fractional distillation until the monomers are free from the traces of dimethacrylates.

Anionic Polymerization of 2 and 3. Lithium chloride (LiCl)[13] and diethylzinc (Et_2Zn)[14,15] improve control of the molecular weights and the MWDs in the anionic polymerizations of (meth)acrylate monomers. Both binary initiator systems (organolithium/LiCl and organopotassium/Et_2Zn) promoted the controlled anionic polymerizations of (meth)acrylates to form long-lived growing species. The added LiCl and Et_2Zn remarkably reduced the propagating rate of (meth)acrylates and lowered the nucleophilicity of active species, probably by interacting with the propagating enolate anions as either a common-ion salt or a weak Lewis acid, respectively. The equilibrium reportedly shifts from the ionic association state toward the nonassociated species in the presence of additives.[14,16] Using these additives, a variety of functional methacrylates[17] including the trialkylsilyl-protected HEMA, **1**,[4] indeed underwent anionic polymerization in a controlled fashion. We therefore employed LiCl and Et_2Zn as additives to realize the living anionic polymerizations of **2** and **3**.

Monomers **2** and **3** were polymerized in THF at −78 °C using either 1,1-diphenyl-3-methylpentyllithium (DMPLi), an adduct of *s*-BuLi and 1,1-diphenylethylene, or diphenylmethylpotassium (Ph_2CHK) as the initiator in both the absence and presence of LiCl and Et_2Zn, respectively. Upon adding the THF solution of monomer to the initiator solution, the red color of the initiator system disappeared immediately to give a colorless solution. The polymerizations of **2** and **3** were homogeneous, and they were quenched with degassed methanol. In several cases, the conversions of monomers were analyzed by ^1H NMR and GLC measurements. The polymers were isolated by precipitating in a large excess of methanol. IR and ^1H and ^{13}C NMR spectroscopies confirmed that the *tert*-butyldimethylsilyl protecting group in the isolated polymers remains intact during the polymerization and workup. The molecular weights of the polymers were determined by end group analysis using the proton signal intensity in the aromatic region of initiator residues in the ^1H NMR spectroscopy as previously reported.[18] The results of the anionic polymerization of **2** and **3** are summarized in Table 1.

The polymerization of **2** proceeded quantitatively with DMPLi in THF at −78 °C for 2 h. The SEC curve of poly(**2**) produced with DMPLi was unimodal with a small tailing toward low molecular weight region, and the polydispersity index, M_w/M_n, was 1.29. The M_n value determined by ^1H NMR measurement was very close to the calculated value based on the molar ratio of monomer to initiator. Similarly, the poly(**2**)s with the predicted molecular weights were obtained in quantitative yields after 2 h by initiating with the binary system of DMPLi and LiCl, supporting the quantitative initiator efficiency.[19] In these cases, 3−5-fold excess of LiCl to DMPLi was added in order to tune the polymerization. The SEC curves of poly(**2**) obtained in the presence of LiCl were significantly narrower, and the M_w/M_n values were approximately 1.05. The MWD was unimodal and very narrow even after the prolonged reaction time of 12 h. This means that there are no intermolecular side reaction such as carbonyl condensation between the propagating chain end and the ester moieties of the resulting polymer. The polymerization of **2** was not complete within 30 min in the presence of LiCl, and the monomer conversions were 57 and 78% after 10 and 30 min reactions, respectively. The polymerizations of other (meth)acrylates were also retarded in the presence of LiCl,[13,16] but they were much faster than the polymerization of **2**. Usually, the complete conversions of (meth)acrylates were attained within several minutes even in the presence of LiCl under the similar polymerization conditions. This indicates that the lower polymerization rate of **2** is probably due to the steric effect of bulky *tert*-butyldimethylsilyl-protected di(ethylene glycol) moiety. The complete consumption of **2** was also achieved with either Ph_2CHK or Ph_2CHK/Et_2Zn at −78 °C for 2 h. The anionic initiators associated with potassium counterion also afforded the poly(**2**)s with controlled molecular weights in quantitative yields. The MWD was narrower ($M_w/M_n = 1.03$), when the polymerization was performed with Ph_2CHK in the presence of Et_2Zn, than in its absence ($M_w/M_n = 1.14$).

The anionic polymerization of **3** using DMPLi in THF at −78 °C for 16 h quantitatively produced poly(**3**) with the predicted M_n and relatively narrow MWD ($M_w/M_n = 1.19$). In the presence of LiCl, poly(**3**) was obtained in 66% and 90% yield after 10 min and 2 h, respectively. The polymerization of **3** is slower than that of **2**, since 100% conversion of **2** is attained after 2 h under

Table 1. Anionic Polymerization of 2 and 3 in THF at −78 °C

run	monomer type, mmol	initiator type, mmol	additive type, mmol	time, h	yield, %	$M_n \times 10^{-3}$		M_w/M_n[c]	tacticity (%)[d]		
						calcd[a]	obsd[b]		*mm*	*mr*	*rr*
1	**2**, 3.63	*s*-BuLi, 0.0811/DPE,[e] 0.306		2	100	13	15	1.29	<1	25	75
2	**2**, 3.63	*s*-BuLi, 0.0744/DPE, 0.301	LiCl, 0.414	10 min	57[f]	8.2	8.1	1.03			
3	**2**, 3.38	*s*-BuLi, 0.0941/DPE, 0.264	LiCl, 0.364	30 min	78[f]	8.3	9.5	1.03			
4	**2**, 2.14	*s*-BuLi, 0.104/DPE, 0.133	LiCl, 0.602	2	100	6.2	5.5	1.03			
5	**2**, 4.98	*s*-BuLi, 0.142/DPE, 0.188	LiCl, 0.535	2	100	10	9.3	1.02	<1	25	75
6	**2**, 4.22	*s*-BuLi, 0.0616/DPE, 0.122	LiCl, 0.302	8	100	20	22	1.05			
7	**2**, 7.76	*s*-BuLi, 0.0471/DPE, 0.118	LiCl, 0.306	12	100	48	63	1.03	<1	25	75
8	**2**, 3.23	Ph_2CHK,[g] 0.113		2	100	8.4	8.0	1.14	14	55	31
9	**2**, 3.14	Ph_2CHK, 0.121	Et_2Zn, 2.52	2	100	7.6	7.5	1.03	14	55	31
10	**3**, 3.18	*s*-BuLi, 0.0746/DPE, 0.239		16	100	14	14	1.19	<1	26	74
11	**3**, 1.92	*s*-BuLi, 0.0770/DPE, 0.301	LiCl, 0.388	10 min	66[f]	5.5	5.7	1.03			
12	**3**, 2.95	*s*-BuLi, 0.0930/DPE, 0.189	LiCl, 0.499	2	90[f]	9.5	10	1.03			
13	**3**, 3.12	*s*-BuLi, 0.0788/DPE, 0.107	LiCl, 0.306	24	100	13	11	1.11	<1	28	72
14	**3**, 2.61	*s*-BuLi, 0.0508/DPE, 0.0839	LiCl, 0.245	24	100	17	17	1.08			
15	**3**, 3.05	Ph_2CHK, 0.0859		24	100	12	11	1.32	7	57	36
16	**3**, 3.84	Ph_2CHK, 0.138	Et_2Zn, 1.13	2	91	7.8	7.3	1.03			
17	**3**, 2.17	Ph_2CHK, 0.0808	Et_2Zn, 1.06	3	100	9.1	8.4	1.03			
18	**3**, 3.29	Ph_2CHK, 0.0841	Et_2Zn, 2.52	24	100	13	13	1.06	6	58	36

[a] M_n(calcd) = (MW of monomer) × [M]/[I] × yield/100 + MW of initiator. [b] M_n(obsd) was determined by end group analysis using ^{1}H NMR. [c] M_w/M_n was determined by SEC calibration using poly(MMA) standards in THF. [d] The triad tacticity was determined by the ^{13}C NMR signal intensity of α-methyl carbon (mm = 22.7−23.7 ppm, mr = 20.2−21.4 ppm, and rr = 18.5−19.5 ppm) of the deprotected polymers. [e] 1,1-Diphenylethylene. [f] Conversion determined by ^{1}H NMR. [g] Diphenylmethylpotassium.

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

run	initiator	first monomer, $[M_1]$/[initiator]	second monomer, $[M_2]$/[initiator]	block copolymer (homopolymer[b])			
				yield, %	$10^{-3}M_n$		M_w/M_n
					calcd	obsd[c]	
19	Ph_2CHK[d]	**2**, 30.0	tBMA, 63.1	100 (98)	18 (8.8)	18 (8.9)	1.03 (1.03)
20	Ph_2CHK[d]	**3**, 12.0	tBMA, 43.1	100 (100)	10 (4.2)	9.0 (3.4)	1.03 (1.05)
21	*s*-BuLi	styrene, 11.0[e]	**2**, 53.0	100	17	17	1.04
22	*s*-BuLi	styrene, 19.2[e]	**3**, 35.2	100	14	15	1.04

[a] Polymerization time: 2 h for **2**; 3 h for **3**; 1 h for tBMA; 20 min for styrene. [b] Homopolymers were obtained at the first-stage polymerization of first monomer. [c] M_ns of the block copolymers were determined by using the M_ns of the homopolymers and the molar ratios of monomer units in the block copolymer analyzed by ^{1}H NMR. [d] A 10-fold excess of Et_2Zn was added to Ph_2CHK before the polymerization of first monomer. [e] A 2-fold excess of 1,1-diphenylethylene and a 5-fold excess of LiCl were added to the living anionic polystyrene before the addition of second monomer.

identical conditions. For the complete conversion of **3**, the polymerization time was prolonged to 24 h. Similar to the polymerization behavior of **2**, the addition of LiCl narrowed the MWDs of poly(**3**)s, while keeping the controlled molecular weights. As expected, the binary initiator system of Ph_2CHK/Et_2Zn provided the excellent molecular weight control and the extremely narrow MWD (M_w/M_n < 1.06) of the resulting polymers. Ph_2CHK by itself gave poly(**3**) with rather broad MWD, whereas the M_n values agreed with the value calculated from the monomer-to-initiator ratio.

We attempted to estimate the stereoregularity of the resulting poly(**2**) and poly(**3**) by ^{1}H and ^{13}C NMR spectroscopies. However, the appropriate signals were overlapped with those of the *tert*-butyldimethylsilyl protecting group. Therefore, we quantitatively converted the poly(**2**) and poly(**3**) into their deprotected forms, poly(DEGMA) and poly(TEGMA), under mild acidic conditions, as shown later. The stereoregularity of the deprotected poly(DEGMA) and poly(TEGMA) could be evaluated independently by the ^{1}H (α-methyl proton) and ^{13}C NMR (carbonyl, quaternary, and α-methyl carbons) spectroscopies, with comparable values. The triad tacticities obtained by the relative signal intensity of α-methyl carbons are shown in Table 1. In the polymerizations using organolithium initiator, the stereoregularity of polymers were rather syndiotactic ($rr \sim$ 72−75%). The organopotassium initiator always produced *mr*-rich configurations. The triad tacticity thus strongly depends on the counterions of anionic initiators. The LiCl and Et_2Zn additives did not influence stereoregularities of the resulting polymers. This is consistent with previous reports on the anionic polymerizations of other methacrylates in a polar solvent of THF.[13,14] Although the additives affect the polymerization rates of the (meth)acrylates by associating with the propagating chain ends, the stereoregularity of the polymers depends primarily on the nature of the initiator counterions.

Block Copolymerization of 2 and 3. Monomers **2** and **3** were copolymerized sequentially to synthesize tailored block copolymers with well-defined chain architectures, as shown in Table 2. The first-stage polymerization of **2** was performed with Ph_2CHK/Et_2Zn in THF at −78 °C for 2 h, and then *tert*-butyl methacrylate (tBMA) was added to the reaction system. The reaction mixture was allowed to polymerize further for 1 h, and the copolymer was quantitatively obtained after quenching with methanol. Figure 1 shows that the SEC curve of copolymer shifts from that of homopoly(**2**) toward the higher molecular weight region while maintaining its unimodal and narrow shape. The composition of each polymer segment estimated by ^{1}H NMR agreed with the feed molar ratio of **2** and tBMA. The M_n values of copolymer were consistent with the calculated values from the monomer-to-initiator ratios. This demonstrates that the propagating carbanion of poly(**2**) is sufficiently stable to initiate the polymerization of tBMA with

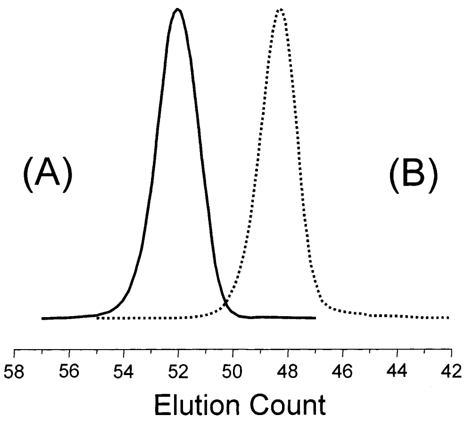
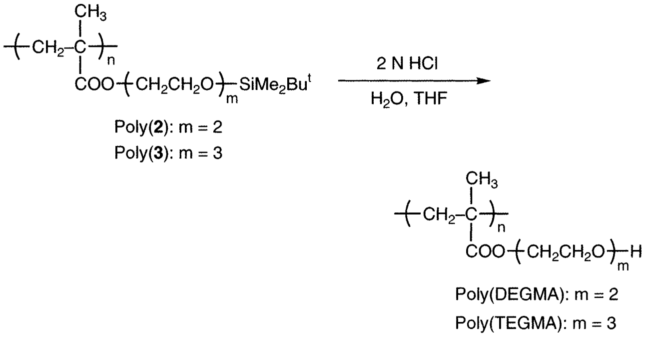


Figure 1. SEC curves of poly(**2**) (peak A, $M_n = 8900$, $M_w/M_n = 1.03$) and poly(**2**)-*block*-poly(tBMA) (peak B, $M_n = 18{,}000$, $M_w/M_n = 1.03$) measured in THF.

Scheme 2



quantitative efficiency to give a poly(**2**)-*block*-poly(tBMA) with the predicted compositions and molecular weight, and with narrow MWD. In a similar manner, a well-defined diblock copolymer of **3** and tBMA was produced with Ph_2CHK/Et_2Zn in quantitative yield. The results obtained here and in the preceding section show the living character of the polymerizations of **2** and **3** under the reaction conditions employed here, similar to the previous polymerization result of **1**.[4] The *tert*-butyldimethylsilyl protecting group effectively masks the OH functionalities and suppresses the serious side reactions during the anionic polymerizations of **1**−**3**.

We next polymerized **2** as a second monomer to synthesize the block copolymer with styrene. The anionic living polystyrene was first synthesized by initiation with *s*-BuLi in THF at −78 °C, and then THF solutions of both 1,1-diphenylethylene and LiCl were added in order to decrease the nucleophilicity of the terminal benzylic carbanion of living polystyrene. Finally, monomer **2** in THF was added at −78 °C to the living polystyrene capped with 1,1-diphenylethylene in the presence of LiCl. The diblock copolymer, polystyrene-*block*-poly(**2**), with predetermined composition and narrow MWD was obtained in quantitative yield. Similarly, sequential block copolymerization of styrene and **3** smoothly proceeded with *s*-BuLi to give a well-defined block copolymer. These results open the synthetic pathway to the tailored amphiphilic block copolymer containing poly(DEGMA) or poly(TEGMA) segment by the sequential anionic copolymerization and the subsequent acidic hydrolysis of poly(**2**) or poly(**3**) segment, as described below.

Deprotection of *tert*-Butyldimethylsilyl Group in Poly(2)−(3). The deprotections of *tert*-butyldimethylsilyl ether linkage of poly(**2**)−(**3**) were carried out to regenerate the OH functionalities by treating with 2 N HCl in aqueous THF at 0 °C for 2 h, as shown in Scheme 2. After the acidic hydrolyses, the deprotected polymers were obtained in good yields. The completion of the hydrolysis could be monitored by ^1H and ^{13}C NMR and IR measurements. In the ^1H NMR spectrum of the both hydrolyzed polymers, the strong proton signals due to $SiC(CH_3)_3$ (0.9 ppm) and $SiCH_3$ (0.1 ppm) completely

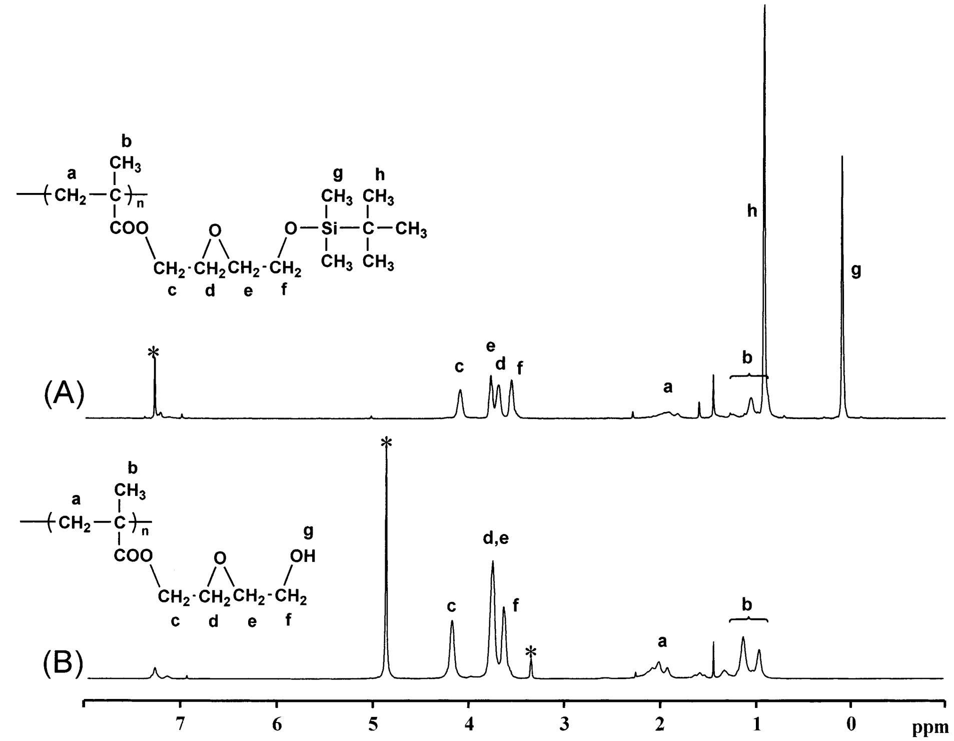
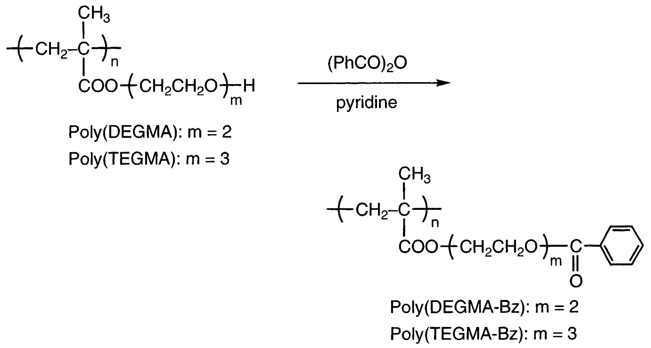


Figure 2. ^1H NMR spectra of poly(**2**) (A) in $CDCl_3$ and poly(DEGMA) (B) in CD_3OD. The signals attributable to solvents are marked with asterisks (∗).

Scheme 3



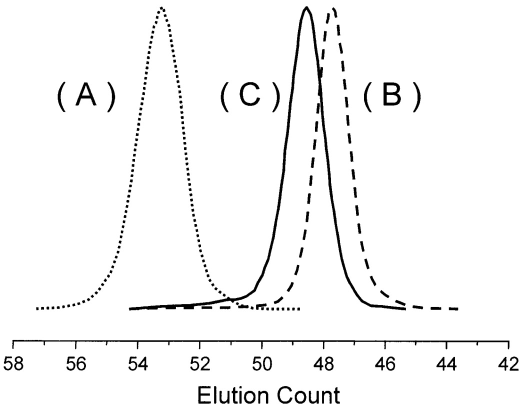


Figure 3. SEC curves of poly(**2**) (peak A, M_n (SEC) = 3300, M_w/M_n = 1.06, DP(NMR) = 46.4), poly(DEGMA) (peak B, M_n(SEC) = 23 000, M_w/M_n = 1.03, DP(NMR) = 50.0), and benzoylated poly(DEGMA) (peak C, M_n(SEC) = 19 000, M_w/M_n = 1.04, DP(NMR) = 51.0) measured in DMF containing 0.01 M LiBr.

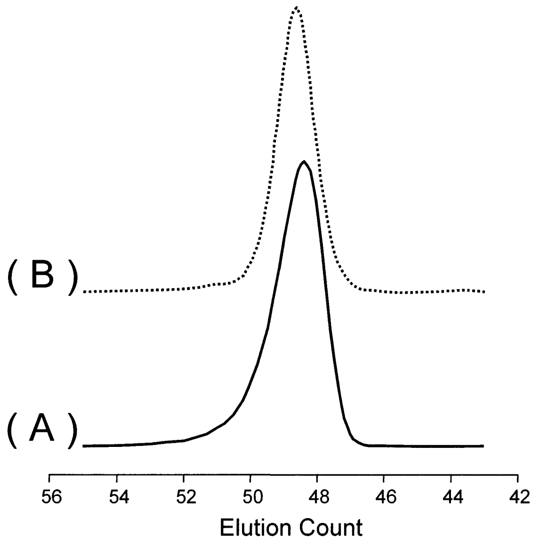


Figure 4. SEC curves of poly(**2**) (peak A, M_n = 14 000, M_w/M_n = 1.06) and benzoylated poly(DEGMA) (peak B, M_n = 14 000, M_w/M_n = 1.02) measured in THF.

disappeared. Figure 2 shows the ^{1}H NMR spectra of poly(**2**) and its hydrolyzed polymer. The proton signals corresponding to the oxyethylene units are observed at 3.6−4.2 ppm after deprotection, while the shape of signals has changed. Their observed intensity relative to other signals revealed that the cleavage exclusively occurred on the Si−O linkage but not on the ester moiety. This is also supported by the fact that no trace of carbon signals at 26 (Si(C(CH$_3$)$_3$), 18 (Si(C(CH$_3$)$_3$), and −5 ppm (SiCH$_3$) was detected in the ^{13}C NMR spectrum of the polymers obtained after hydrolyses. Furthermore, the IR absorptions at 777, 836, and 940 cm^{-1} due to the stretching and deformation vibration of Si−O−C and Si−CH$_3$ linkages disappeared and a broad absorption characteristic for the OH groups newly appeared at 3100−3700 cm^{-1} after hydrolyses. These spectroscopic observations substantiate the point that complete removals of the *tert*-butyldimethylsilyl protecting groups in poly(**2**) and poly(**3**) are attained to form poly(DEGMA) and poly(TEGMA) under acidic conditions, as has been reported in the transformation of poly(**1**) into poly(HEMA).[4] The quantitative deprotection of poly(**2**) and poly(**3**) also occurred under the neutral conditions by treating with Bu$_4$NF in THF at room temperature for 2 h, as expected.[12]

We have examined the SEC measurement of the resulting poly(DEGMA) in DMF containing 0.01 M LiBr, because it was insoluble in THF. Parts A and B of Figure 3 show the typical SEC curves of the poly(**2**) and the poly(DEGMA) after hydrolysis, respectively. Very interestingly, the SEC curve of poly(DEGMA) shifts toward higher molecular weight region after the acid hydrolysis with keeping their unimodal and narrow shape, although the molecular weight of the deprotected polymer theoretically decreases after the removal of *tert*-butyldimethylsilyl protecting group. In fact, the degree of polymerization of poly(DEGMA) estimated by the ^{1}H NMR (DP = 50.0) was in accordance with that of poly(**2**) (DP = 46.4) within the experimental error. The elution behavior in SEC is probably due to the difference in the hydrodynamic volume of the polymers before and after deprotection in a highly polar DMF solvent. Similar phenomenon was also observed during the course of the hydrolysis of poly(**3**) to poly(TEGMA). To further confirm the MWD of polymers after the hydrolysis, we quantitatively converted the polar OH groups of poly(DEGMA) and poly(TEGMA) into their benzoyl ester forms, poly(DEGMA-Bz) and poly(TEGMA-Bz), by the reaction with benzoic anhydride in pyridine, as shown in Scheme 3. ^{1}H NMR analysis revealed that the degree of polymerization of poly(DEGMA-Bz) (DP = 51.0) again agreed with the value of poly(DEGMA) (DP = 50.0). The SEC curve of the poly(DEGMA-Bz) again shows a narrow MWD, as can be seen in Figure 3C. The chromatogram slightly shifts from that of poly(DEGMA) toward the lower molecular weight side in DMF, although the theoretical molecular weight increases via the benzoylation of OH group. The poly(TEGMA-Bz) also shows a unimodal SEC curve and a similar elution behavior in DMF solution. The resulting benzoate polymers were soluble in THF, and we measured their SEC in THF solution. Figure 4 shows the SEC curves of poly(**2**) and poly(DEGMA-Bz) obtained after a two-step polymer reaction using the acidic hydrolysis and the following benzoylation. The poly(DEGMA-Bz) elutes at the reasonable molecular weight region in THF solution. More importantly, the SEC curve possesses unimodal and narrow shape similar to the chromatogram obtained in DMF, indicating that no side reaction such as main chain degradation and/or cross-linking takes place during the course of deprotection and benzoylation. We have thus realized that the poly(DEGMA) and poly(TEGMA) obtained after deprotections maintain linear and well-defined structures similar to the parent protected polymers. The acidic hydrolysis of poly(**2**) and poly(**3**) segments in the block

Table 3. Solubility of Polymers[a]

solvent	poly (**2**)[b]	poly (**3**)[c]	poly (DEGMA)[d]	poly (TEGMA)[e]	poly (HEMA)[f]	poly (MMA)[g]
hexane	S	S	I	I	I	I
benzene	S	S	I	I	I	S
$CHCl_3$	S	S	S	S	I	S
acetone	S	S	I	S	I	S
ethyl acetate	S	S	I	S	I	S
Et_2O	S	S	I	I	I	I
1,4-dioxane	S	S	S	S	I	S
THF	S	S	I	I	I	S
DMF	S	S	S	S	S	S
DMSO	S	S	S	S	S	S
EtOH	S	S	S	S	S	I
MeOH	I	I	S	S	S	I
water	I	I	S	S	I	I

[a] Key: I, insoluble; S, soluble. All polymer samples were synthesized with *s*-BuLi/DPE/LiCl in THF at −78 °C. [b] M_n = 20 000, M_w/M_n = 1.05. [c] M_n = 19 000, M_w/M_n = 1.08. [d] M_n = 7300, M_w/M_n = 1.03. [e] M_n = 7000, M_w/M_n = 1.05. [f] Poly(2-hydroxyethyl methacrylate), M_n = 10 000, M_w/M_n = 1.03. [g] Poly(methyl methacrylate), M_n = 20 000, M_w/M_n = 1.03.

copolymers similarly proceeded to give a series of amphiphilic block copolymers such as poly(DEGMA)-*block*-poly(tBMA), poly(TEGMA)-*block*-poly(tBMA), polystyrene-*block*-poly(DEGMA), and polystyrene-*block*-poly(TEGMA).

Solubility and Glass Transition Temperature of Polymers. The solubilities of polymers obtained in this study are shown in Table 3 with those of poly(HEMA) and poly(MMA) as the references. Poly(**2**) and poly(**3**) were insoluble in methanol and water but soluble in a wide range of organic solvents including hexane and ethanol, indicating their amphiphilic characters. The solubilities of polymers drastically changed after deprotection. The resulting poly(DEGMA) and poly(TEGMA) became insoluble in nonpolar solvents such as hexane, benzene, and diethyl ether, as expected. Most importantly, the both polymers showed excellent solubility in water, in sharp contrast to the fact that poly(HEMA) was not soluble in water. The observed changes in solubility mean that the polarity of the deprotected polymers remarkably increase during the transformations of silyl ethers to OH moieties. Hence, it is demonstrated that the pendant di(ethylene glycol) and tri(ethylene glycol) units in poly(DEGMA) and poly(TEGMA) induce the water solubility and the hydrophilicity higher than the poly(HEMA) bearing shorter ethylene glycol unit.

All of the polymers obtained in this study were colorless and sticky, and their glass transition temperatures (T_gs) were measured by differential scanning calorimetry (DSC). Poly(**2**), poly(**3**), poly(DEGMA), and poly(TEGMA) presented T_g values of −83, −87, −95, and −130 °C, respectively. The flexible oligo(ethylene glycol) moieties in each monomer unit may afford these very low T_g values.

In conclusion, we have succeeded in the anionic living polymerizations of *tert*-butyldimethylsilyl-protected oligo(ethylene glycol) methacrylates, **2** and **3**, to give polymers having well-defined primary chain structures including narrow MWDs and tailored M_ns. The water-soluble polymethacrylates, poly(DEGMA) and poly(TEGMA), are readily obtained by the subsequent deprotections of the resulting polymers under the mild acidic conditions.

Experimental Section

Materials. All reagents were purchased from Tokyo Kasei, unless otherwise stated, and purified in the usual manner. Commercially available methacryloyl chloride and *tert*-butyldimethylsilyl chloride (Aldrich) were used without purification. Di(ethylene glycol) and tri(ethylene glycol) (Koso Chemical) were dried and distilled over CaH_2 under the reduced pressure. Triethylamine, pyridine, and dichloromethane were dried and distilled over CaH_2. LiCl (Wako Pure Chemical) was dried in vacuo for 2 days under heating and used as a THF solution. Diethylzinc (Tosoh-Akzo) was distilled under the reduced pressure and diluted with dry THF. Trioctylaluminum (Sumitomo Chemical Industry) was diluted with dry heptane. Styrene was washed with 10% aqueous NaOH solution and water and dried over anhydrous $MgSO_4$. It was then dried and distilled over CaH_2 in vacuo and finally distilled from the THF solution of benzylmagnesium chloride on a vacuum line. *tert*-Butyl methacrylate was distilled over CaH_2 and then distilled in the presence of trioctylaluminum (1 mol %) on a vacuum line. 1,1-Diphenylethylene was distilled from CaH_2 in vacuo and then distilled in the presence of 1,1-diphenylhexyllithium on a vacuum line. THF as the polymerization solvent was refluxed over sodium wire, distilled over $LiAlH_4$ under nitrogen, and finally distilled from sodium naphthalenide solution on a vacuum line. Heptane was washed with concentrated H_2SO_4 and dried over anhydrous $MgSO_4$, and it was dried over P_2O_5 for 1 day under reflux. It was then distilled in the presence of *n*-BuLi under nitrogen.

Initiators. Commercially available *s*-BuLi (1.3 M in cyclohexane, Nacalai Tesque Inc.) was used without purification and diluted with dry heptane. Diphenylmethylpotassium was prepared by the reaction of potassium naphthalenide with a 1.1-fold excess of diphenylmethane in THF at room temperature for 48 h.[20] The concentrations of initiators were determined by colorimetric titration using standardized 1-octanol in THF in a sealed reactor in vacuo as previously reported.[21]

Di(ethylene glycol) *tert*-Butyldimethylsilyl Ether (DEG-Si). A solution of *tert*-butyldimethylsilyl chloride (5.80 g, 38.7 mmol) in dichloromethane (30 mL) was added dropwise to a mixture of di(ethylene glycol) (33.0 g, 307 mmol), pyridine (24.8 g, 314 mmol), and dichloromethane (60 mL) at 0 °C under nitrogen. The mixture was stirred for 12 h at room temperature and concentrated under reduced pressure. Hexane (100 mL) was added to the residue to give two phases. The resulting DEG-Si and the corresponding disilyl ether were extracted from an excess of di(ethylene glycol) with hexane five times. The combined hexane layer was concentrated in vacuo and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 10/1 to 4/1) to give pure DEG-Si (6.91 g, 31.4 mmol, 81%) as a colorless liquid. The resulting DEG-Si was used directly for the following reaction without further purification. ^{1}H NMR (C_6D_6): δ 0.04 (s, 6H, SiCH_3), 0.95 (s, 9H, Si−C−CH_3), 2.27 (s, 1H, OH), 3.26−3.33 (m, 4H, $OCH_2CH_2OCH_2CH_2OSi$), 3.52 (t, 2H, J = 5 Hz, HOCH_2), 3.57 (t, 2H, J = 5 Hz, CH_2OSi). ^{13}C NMR (C_6D_6): δ −5.3 (SiCH_3), 18.7 (Si−C−CH_3), 26.3 (Si−C−CH_3), 62.1 (HOCH_2), 63.2 (CH_2OSi), 72.9 and 73.0 ($OCH_2CH_2OCH_2CH_2OSi$). IR (neat, cm^{-1}): 777, 834, 940, 1068, 1107, 1255, 1463, 2858, 2929, 2955, 3200−3600 (OH). Anal. Calcd for $C_{10}H_{24}O_3Si$: C, 54.50, H, 10.98. Found: C, 54.32, H, 10.83.

2-[2-[(*tert*-Butyldimethylsilyl)oxy]ethoxy]ethyl Methacrylate (2). A solution of methacryloyl chloride (5.22 g, 49.7 mmol) in ether (30 mL) was added dropwise to a mixture of DEG-Si (7.13 g, 32.4 mmol), triethylamine (6.79 g, 67.2 mmol), and ether (80 mL) with stirring at 0 °C under nitrogen. The reaction mixture was stirred overnight at room temperature and filtered to remove a precipitated triethylamine hydrochloride. The filtrate was washed with 10% aqueous NaOH solution three times and dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated under the reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 10/1 to 10/3). Vacuum distillation in the presence of a trace amount of methylene blue gave a colorless liquid of **2** (7.20 g, 24.9 mmol, 77%, bp 86−88

°C/0.25 mmHg). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.04 (s, 6H, $\mathrm{SiC}H_3$), 0.95 (s, 9H, $\mathrm{Si{-}C{-}C}H_3$), 1.83 (s, 3H, α-$\mathrm{C}H_3$), 3.29 (t, 2H, J = 5 Hz, $\mathrm{OC}H_2\mathrm{CH_2OSi}$), 3.35 (t, 2H, J = 5 Hz, $\mathrm{COOCH_2C}H_2\mathrm{O}$), 3.59 (t, 2H, J = 5 Hz, $\mathrm{OCH_2C}H_2\mathrm{OSi}$), 4.14 (t, 2H, J = 5 Hz, $\mathrm{COOC}H_2\mathrm{CH_2O}$), 5.20 and 6.16 (2s, 2H, $\mathrm{C}H_2{=}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ −5.2 ($\mathrm{Si}C\mathrm{H_3}$), 18.6 (α-$C\mathrm{H_3}$), 18.7 ($\mathrm{Si{-}}C\mathrm{{-}CH_3}$), 26.3 ($\mathrm{Si{-}C{-}}C\mathrm{H_3}$), 63.2 ($C\mathrm{H_2OSi}$), 64.0 ($\mathrm{COO}C\mathrm{H_2}$), 69.3 ($\mathrm{COOCH_2}C\mathrm{H_2O}$), 72.8 ($\mathrm{O}C\mathrm{H_2CH_2OSi}$), 125.3 ($C\mathrm{H_2}{=}$), 136.8 ($\mathrm{CH_2{=}}C$), 166.9 ($C{=}\mathrm{O}$). IR (neat, cm^{-1}): 777, 836, 940, 1048, 1111, 1147, 1168, 1255, 1297, 1320, 1463, 1473, 1641, 1722 (C=O), 2853, 2931, 2956. Anal. Calcd for $\mathrm{C_{14}H_{28}O_4Si}$: C, 58.29, H, 9.78. Found: C, 58.22, H, 9.94.

Tri(ethylene glycol) *tert*-Butyldimethylsilyl Ether (TEG-Si). A procedure similar to that described above for DEG-Si was followed using tri(ethylene glycol) (37.8 g, 250 mmol), *tert*-butyldimethylsilyl chloride (5.80 g, 38.7 mmol), and pyridine (27.0 g, 342 mmol). Column chromatography (silica gel, hexane/ethyl acetate = 10/1−3/1) gave TEG-Si (7.40 g, 31.2 mmol, 73%) as a colorless liquid. The resulting TEG-Si was directly used for the following reaction without further purification. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.05 (s, 6H, $\mathrm{SiC}H_3$), 0.95 (s, 9H, $\mathrm{Si{-}C{-}C}H_3$), 3.18 (s, 1H, $\mathrm{O}H$), 3.46−3.53 (m, 8H, $\mathrm{OCH_2C}H_2\mathrm{OC}H_2\mathrm{C}H_2\mathrm{OC}H_2\mathrm{CH_2OSi}$), 3.72−3.79 (m, 4H, $\mathrm{HOC}H_2$, and $\mathrm{C}H_2\mathrm{OSi}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ −5.4 ($\mathrm{Si}C\mathrm{H_3}$), 18.7 ($\mathrm{Si{-}}C\mathrm{{-}CH_3}$), 26.3 ($\mathrm{Si{-}C{-}}C\mathrm{H_3}$), 62.1 ($\mathrm{HO}C\mathrm{H_2}$), 63.2 ($C\mathrm{H_2OSi}$), 70.8, 71.2, 73.0, and 73.1 ($\mathrm{OCH_2}C\mathrm{H_2O}C\mathrm{H_2}C\mathrm{H_2O}C\mathrm{H_2CH_2OSi}$). IR (neat, cm^{-1}): 777, 836, 937, 1111, 1142, 1255, 1464, 1473, 2858, 2929, 2953, 3100−3600 (OH). Anal. Calcd for $\mathrm{C_{12}H_{28}O_4Si}$: C, 54.51, H, 10.67. Found: C, 53.99, H, 10.19.

2-[2-[2-[(*tert*-Butyldimethylsilyl)oxy]ethoxy]ethoxy]ethyl Methacrylate (3). The same procedure was followed as described above for **2** using methacryloyl chloride (5.11 g, 48.7 mmol), triethylamine (9.83 g, 97.4 mmol), and TEG-Si (7.82 g, 32.6 mmol) in place of DEG-Si. The product was purified by column chromatography (silica gel, hexane/ethyl acetate = 10/1 to 10/3) and the subsequent vacuum distillation in the presence of methylene blue to afford a colorless liquid of **3** (8.76 g, 26.4 mmol, 81%, bp 106−110 °C/0.3 mmHg). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.06 (s, 6H, $\mathrm{SiC}H_3$), 0.96 (s, 9H, $\mathrm{Si{-}C{-}C}H_3$), 1.82 (s, 3H, α-$\mathrm{C}H_3$), 3.37 (m, 8H, $\mathrm{OCH_2C}H_2\mathrm{OC}H_2\mathrm{C}H_2\mathrm{OC}H_2\mathrm{CH_2OSi}$), 3.64 (t, 2H, J = 5 Hz, $\mathrm{C}H_2\mathrm{OSi}$), 4.15 ($\mathrm{COOC}H_2$), 5.19 and 6.15 (2s, 2H, $\mathrm{C}H_2{=}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ −5.1 ($\mathrm{Si}C\mathrm{H_3}$), 18.4 (α-$C\mathrm{H_3}$), 18.5 ($\mathrm{Si{-}}C\mathrm{{-}CH_3}$), 26.1 ($\mathrm{Si{-}C{-}}C\mathrm{H_3}$), 63.1 ($\mathrm{SiO}C\mathrm{H_2}$), 64.0 ($\mathrm{COO}C\mathrm{H_2}$), 69.3, 70.9, 71.0, and 73.0 ($\mathrm{OCH_2}C\mathrm{H_2O}C\mathrm{H_2}C\mathrm{H_2O}C\mathrm{H_2CH_2OSi}$), 125.2 ($C\mathrm{H_2}{=}$), 136.8 ($\mathrm{CH_2{=}}C$), 166.9 ($C{=}\mathrm{O}$). IR (neat, cm^{-1}): 777, 836, 940, 1105, 1147, 1168, 1255, 1298, 1320, 1463, 1641, 1722 (C=O), 2857, 2931, 2955. Anal. Calcd for $\mathrm{C_{16}H_{32}O_5Si}$: C, 57.80, H, 9.70. Found: C, 57.73, H, 9.82.

Purification of Monomers. After careful fractional distillation, monomers **2** and **3** were degassed and sealed off in an apparatus equipped with a break-seal in the presence of $\mathrm{CaH_2}$ and diluted with dry heptane. The monomer solution in heptane was stirred for 20 h at room temperature and distilled from $\mathrm{CaH_2}$ on a vacuum line into ampules fitted with break-seals. The distilled monomers were treated with 1−2 mol % of trioctylaluminum in heptane for 10 min and again distilled under high vacuum conditions. The purified monomers were finally distilled in vacuo into an ampule fitted with a break-seal and diluted with dry THF. The resulting monomer solutions (0.2−0.3 M) in THF were stored at −30 °C until ready to use for the anionic polymerization.

Polymerization Procedures. All polymerizations were carried out at −78 °C in an all-glass apparatus equipped with break-seals under high vacuum conditions as previously reported.[21] A typical polymerization procedure was as follows: A THF solution (2.51 mL) of 1,1-diphenylethylene (0.188 mmol) was added to a heptane solution (4.33 mL) of *s*-BuLi (0.142 mmol) through the break-seal at −78 °C. After 10 min, LiCl (0.535 mmol) in THF (3.69 mL) was added to the mixture at −78 °C, and the initiator system was allowed to stand at −78 °C for 10 min. Then, monomer **2** (4.98 mmol) in THF (20.5 mL) was rapidly added to the initiator system at −78 °C through the break-seal with vigorous shaking of the apparatus. After the reaction was allowed to stand at −78 °C for 2 h, the polymerization was terminated with degassed methanol. After concentration of the reaction mixture in vacuo, the residue was poured into a large excess of methanol to precipitate poly(**2**) (1.46 g, 100%, M_n = 9300, $M_\mathrm{w}/M_\mathrm{n}$ = 1.02).

Poly(**2**) and poly(**3**) were further purified by reprecipitations in a THF/methanol system and by freeze-drying from benzene solution. Polymers thus obtained were characterized by ^{1}H and ^{13}C NMR and IR spectroscopies. The following is the full list.

Poly(2). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.11 (s, 6H, $\mathrm{SiC}H_3$), 0.94 (s, 9H, $\mathrm{Si{-}C{-}C}H_3$), 0.9−1.2 (m, 3H, α-$\mathrm{C}H_3$), 1.8−2.1 (br, 2H, $\mathrm{C}H_2$), 3.56 (bs, 2H, $\mathrm{OC}H_2\mathrm{CH_2OSi}$), 3.70 (bs, 2H, $\mathrm{COOCH_2C}H_2\mathrm{O}$), 3.79 (bs, 2H, $\mathrm{C}H_2\mathrm{CH_2OSi}$), 4.10 (bs, 2H, $\mathrm{COOC}H_2\mathrm{CH_2O}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ −5.1 ($\mathrm{Si}C\mathrm{H_3}$), 18.4 ($\mathrm{Si{-}}C\mathrm{{-}CH_3}$), 18−20 (α-$C\mathrm{H_3}$), 26.1 ($\mathrm{Si{-}C{-}}C\mathrm{H_3}$), 45 (main chain quarternary), 54 (main chain $C\mathrm{H_2}$), 62.9 ($\mathrm{O}C\mathrm{H_2CH_2OSi}$), 63.9 ($\mathrm{COO}C\mathrm{H_2}$), 68.7 ($\mathrm{COOCH_2}C\mathrm{H_2O}$), 72.7 ($C\mathrm{H_2OSi}$), 177 ($C{=}\mathrm{O}$). IR (KBr, cm^{-1}): 777, 836, 940, 1108, 1147, 1253, 1733 (C=O), 2856, 2929, 2952.

Poly(3). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.10 (s, 6H, $\mathrm{SiC}H_3$), 0.93 (s, 9H, $\mathrm{Si{-}C{-}C}H_3$), 0.9−1.2 (m, 3H, α-$\mathrm{C}H_3$), 1.8−2.2 (br, 2H, $\mathrm{C}H_2$), 3.58 (t, J = 5 Hz, 2H, $\mathrm{OCH_2C}H_2\mathrm{OSi}$), 3.66 (bs, 4H, $\mathrm{OCH_2CH_2OC}H_2\mathrm{C}H_2\mathrm{OCH_2CH_2OSi}$), 3.69 (bs, 2H, $\mathrm{COOCH_2C}H_2\mathrm{O}$), 3.79 (t, J = 5 Hz, 2H, $\mathrm{C}H_2\mathrm{CH_2OSi}$), 4.11 (bs, 2H, $\mathrm{COOC}H_2\mathrm{CH_2O}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ = −5.1 ($\mathrm{Si}C\mathrm{H_3}$), 18.5 ($\mathrm{Si{-}}C\mathrm{{-}CH_3}$), 17−20 (α-$C\mathrm{H_3}$), 26.1 ($\mathrm{Si{-}C{-}}C\mathrm{H_3}$), 45 (main chain quarternary), 54 (main chain $C\mathrm{H_2}$), 62.7 ($\mathrm{O}C\mathrm{H_2CH_2OSi}$), 63.8 ($\mathrm{COO}C\mathrm{H_2}$), 68.5 ($\mathrm{COOCH_2}C\mathrm{H_2O}$), 70.6 and 70.8 ($\mathrm{OCH_2CH_2O}C\mathrm{H_2}C\mathrm{H_2OCH_2CH_2OSi}$), 72.7 ($C\mathrm{H_2OSi}$), 177 ($C{=}\mathrm{O}$). IR (KBr, cm^{-1}): 777, 836, 940, 1111, 1147, 1253, 1463, 1473, 1733 (C=O), 2858, 2929, 2957.

Deprotection of Polymers. Two methods were used to remove *tert*-butyldimethylsilyl protecting group of poly(**2**) and poly(**3**) with either $\mathrm{Bu_4NF}$ or aqueous HCl in THF. The typical procedures using poly(**2**) were shown below.

Method A. $\mathrm{Bu_4NF}$ (10 mL of a 1 M THF solution) was added dropwise to poly(**2**) (0.21 g, 0.73 mmol based on the monomer unit) at room temperature, and the solution was stirred for 2 h. After concentration under reduced pressure, the residue was dissolved in ethanol, and the solution was poured into a large excess of hexane. The complete removal of the trialkylsilyl group was clarified by the ^{1}H NMR measurement of the resulting polymer.

Method B. Aqueous 2 N HCl (1 mL) was added dropwise to a solution of poly(**2**) (0.40 g, 1.4 mmol based on the monomer unit, DP = 46.4, $M_\mathrm{w}/M_\mathrm{n}$ = 1.06) in THF (10 mL) at 0 °C, and the homogeneous mixture was stirred at 0 °C for 2 h. After concentration in vacuo, the deprotected polymer was dissolved in ethanol and then precipitated in hexane. The resulting poly(DEGMA) (0.22 g, 1.3 mmol, 93%, DP = 50.0, $M_\mathrm{w}/M_\mathrm{n}$ = 1.03)) was purified by freeze-drying from 1,4-dioxane containing a small amount of methanol. The deprotection of poly(**3**) was carried out similarly to afford poly(TEGMA) quantitatively. The deprotected polymers were characterized by ^{1}H and ^{13}C NMR and IR measurements as follows.

Poly(DEGMA). ^{1}H NMR ($\mathrm{CD_3OD}$): δ 0.8−1.3 (m, 3H, α-$\mathrm{C}H_3$), 1.8−2.2 (br, 2H, $\mathrm{C}H_2$), 3.62 (bs, 2H, $\mathrm{C}H_2\mathrm{OH}$), 3.74 (bs, 4H, $\mathrm{COOCH_2C}H_2\mathrm{OC}H_2\mathrm{CH_2OH}$), 4.16 (bs, 2H, $\mathrm{COOC}H_2$). ^{13}C NMR ($\mathrm{CD_3OD}$): δ 16−20 (α-$C\mathrm{H_3}$), 44−45 (main chain quarternary), 54 (main chain $C\mathrm{H_2}$), 60.4 ($\mathrm{O}C\mathrm{H_2CH_2OH}$), 63.7 ($\mathrm{COO}C\mathrm{H_2}$), 67.7 ($\mathrm{COOCH_2}C\mathrm{H_2O}$), 71.7 ($C\mathrm{H_2OH}$), 177 ($C{=}\mathrm{O}$). IR (KBr, cm^{-1}): 1037, 1068, 1132, 1162, 1271, 1453, 1728 (C=O), 2876, 2943, 3100−3700 (OH).

Poly(TEGMA). ^{1}H NMR ($\mathrm{CD_3OD}$): δ 0.8−1.3 (m, 3H, α-$\mathrm{C}H_3$), 1.8−2.2 (br, 2H, $\mathrm{C}H_2$), 3.65 (bs, 2H, $\mathrm{C}H_2\mathrm{OH}$), 3.72 (bs, 6H, $\mathrm{COOCH_2CH_2OC}H_2\mathrm{C}H_2\mathrm{OC}H_2\mathrm{CH_2OH}$), 3.8 (bs, 2H, $\mathrm{COOCH_2C}H_2\mathrm{O}$), 4.16 (bs, 2H, $\mathrm{COOC}H_2$). ^{13}C NMR ($\mathrm{CD_3OD}$): δ 16−20 (α-$C\mathrm{H_3}$), 44−45 (main chain quarternary), 54 (main chain $C\mathrm{H_2}$), 60.4 ($\mathrm{O}C\mathrm{H_2CH_2OH}$), 63.4 ($\mathrm{COO}C\mathrm{H_2}$), 67.8 ($\mathrm{COOCH_2}C\mathrm{H_2O}$), 69.6 ($\mathrm{O}C\mathrm{H_2}C\mathrm{H_2O}$), 71.9 ($C\mathrm{H_2OH}$), 177 ($C = \mathrm{O}$). IR (KBr, cm^{-1}): 1068, 1126, 1249, 1728 (C=O), 2875, 2929, 3100−3700 (OH).

Benzoylation of Polymers. Benzoic anhydride (1.85 g, 8.2 mmol) in dry pyridine (2 mL) was added in several portions to a solution of poly(DEGMA) (0.10 g, 0.58 mmol based on the monomer unit, DP = 50.0, $M_\mathrm{w}/M_\mathrm{n}$ = 1.03) in pyridine (3 mL) at 0 °C under nitrogen. The reaction mixture was stirred at room temperature for 24 h. After concentration in vacuo, the residue was dissolved in THF, and the solution was poured into water to precipitate. The resulting polymer was further purified by the reprecipitations from a THF/hexane system and by the freeze-drying from the benzene solution. The yield of the benzoylated poly(DEGMA), poly(DEGMA-Bz) (0.17 g, 0.58 mmol based on the monomer unit, DP = 51.0, $M_w/M_n = 1.04$), was quantitative. The benzoylation of poly(TEGMA) was performed similarly to afford the corresponding benzoylated poly(TEGMA), poly(TEGMA-Bz). The ^{1}H NMR spectra of the resulting polymers indicated that the complete benzoylations of poly(DEGMA) and poly(TEGMA) proceeded as follows.

Poly(DEGMA-Bz). ^{1}H NMR ($CDCl_3$): δ 0.7−1.3 (m, 3H, α-CH_3), 1.6−2.2 (br, 2H, CH_2), 3.68 and 3.76 (2bs, 4H, $COOCH_2CH_2OCH_2CH_2OCOPh$), 4.09 (bs, 2H, $COOCH_2$), 4.44 (bs, 2H, CH_2OCOPh), 7.3−8.2 (m, 5H, aromatic).

Poly(TEGMA-Bz). ^{1}H NMR ($CDCl_3$): δ 0.7−1.3 (m, 3H, α-CH_3), 1.7−2.2 (br, 2H, CH_2), 3.66 and 3.82 (2bs, 8H, $COOCH_2CH_2OCH_2CH_2OCH_2CH_2OCOPh$), 4.09 (bs, 2H, CO-$OCH_2$), 4.47 (bs, 2H, CH_2OCOPh), 7.3−8.2 (m, 5H, aromatic).

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) in C_6D_6, CD_3OD, or $CDCl_3$. Tacticity of poly(DEGMA) and poly(TEGMA) was determined by the ^{13}C NMR integral ratio of three split α-methyl carbon signals appearing at 18.5−23.7 ppm. Three signals were assigned as *mm* (22.7−23.7 ppm), *mr* (20.2−21.4 ppm), and *rr* (18.5−19.5 ppm) triads. Infrared spectra (KBr disk or neat) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. SEC chromatograms for determination of molecular weight distribution were obtained in THF at 40 °C at a flow rate of 1.0 mL min^{-1} with a TOSOH HLC-8020 instrument equipped with a series of polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$, measurable molecular weight range: 2×10^3 to 4×10^6) and with ultraviolet (254 nm) or refractive index detection. SEC measurements ware also performed in DMF containing 0.01 M LiBr at 40 °C at a flow rate of 1.0 mL min^{-1} with a TOSOH HLC-8120 instrument equipped with three polystyrene gel columns (TOSOH GMH$_{XL}$, × 2 and G2000H$_{XL}$, measurable molecular weight range: 10^3 to 4×10^8). The T_gs of the polymers were measured by DSC using a Seiko Instrument DSC220 apparatus, calibrated with indium and tin, and analyzed by a SSC5200TA station. The samples were first heated to 100 °C, cooled rapidly to −150 °C with liquid nitrogen, and then scanned again at a rate of 5 or 10 °C min^{-1}.

Acknowledgment. This research was supported by Grant-in Aid for Scientific Research on Priority Areas, "New Polymers and Their Nano-Organized Systems" (08246102), from the Ministry of Education, Science, Sports, and Culture, Japan. T.I. thanks the Shorai Foundation and Iwatani Foundation for their financial support.

References and Notes

(1) (a) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983. (b) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization*; Marcel Dekker: New York, 1996.

(2) (a) Nakahama, S.; Hirao, A. *Prog. Polym. Sci.* **1990**, *15*, 299. (b) Hirao, A.; Nakahama, S. *Trends Polym. Sci.* **1994**, *2*, 267. (c) Hirao, A.; Loykulnant, S.; Ishizone, T. *Prog. Polym. Sci.* **2002**, *27*, 1399.

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

(4) Mori, H.; Wakisaka, O.; Hirao, A.; Nakahama, S. *Macromol. Chem. Phys.* **1994**, *195*, 3213.

(5) (a) Nojiri, C.; Okano, T.; Grainger, D.; Park, K. D.; Nakahama, S.; Suzuki, K.; Kim, S. W. *Trans. ASAIO* **1987**, *33*, 596. (b) Nojiri, C.; Okano, T.; Koyanagi, H.; Nakahama, S.; Park, K. D.; Kim, S. W. *J. Biomater. Sci., Polym. Ed.* **1992**, *4*, 75.

(6) (a) Senshu, K.; Yamashita, S.; Ito, M.; Hirao, A.; Nakahama, S. *Langmuir* **1995**, *11*, 2293. (b) Senshu, K.; Yamashita, S.; Mori, H.; Ito, M.; Hirao, A.; Nakahama, S. *Langmuir* **1999**, *15*, 1754. (c) Senshu, K.; Kobayashi, M.; Ikawa, N.; Yamashita, S.; Hirao, A.; Nakahama, S. *Langmuir* **1999**, *15*, 1763.

(7) Mori, H.; Hirao, A.; Nakahama, S. *Macromolecules* **1994**, *27*, 35.

(8) Zhang, H.; Ruckenstein, E. *Macromolecules* **2000**, *33*, 4738.

(9) Mori, H.; Hirao, A.; Nakahama, S.; Senshu, K. *Macromolecules* **1994**, *27*, 4093.

(10) Karlsson, J. O.; Gatenholm, P. *Polymer* **1996**, *37*, 4251.

(11) Ore, S.; Kulvik, E.; Ohr, W.; Zapffe, J. W. *Makromol. Chem.* **1971**, *148*, 211.

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

(13) (a) Fayt, R.; Forte, R.; Jacobs, C.; Jérôme, R.; Ouhadi, T.; Teyssié, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442. (b) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1990**, *23*, 2618.

(14) Ozaki, H.; Hirao, A.; Nakahama, S. *Macromol. Chem. Phys.* **1995**, *196*, 2099.

(15) (a) Ishizone, T.; Yoshimura, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1998**, *31*, 8706. (b) Kobayashi, M.; Okuyama, S.; Ishizone, T.; Nakahama, S. *Macromolecules* **1999**, *32*, 6466.

(16) (a) Kunkel, D.; Müller, A. H. E.; Janata, M.; Lochmann, L. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 315. (b) Yakimansky, A. V.; Müller, A. H. E.; Van Beylen, M. *Macromolecules* **2000**, *33*, 5686.

(17) (a) Ozaki, H.; Hirao, A.; Nakahama, S. *Macromolecules* **1992**, *25*, 1391. (b) Hild, G.; Lamps, J. P.; Rempp, P. *Polymer* **1993**, *34*, 2875. (c) Creutz, S.; Teyssié, Ph.; Jérôme, R. *Macromolecules* **1997**, *30*, 6. (d) Ishizone, T.; Uehara, G.; Hirao, A.; Nakahama, S.; Tsuda, K. *Macromol. Chem. Phys.* **1998**, *199*, 1827. (e) Zhang, H.; Ruckenstein, E. *Macromolecules* **1998**, *31*, 746. (f) Ishizone, T.; Sugiyama, K.; Sakano, Y.; Mori, H.; Hirao, A.; Nakahama, S. *Polym. J.* **1999**, *31*, 983. (g) Zhang, H.; Ruckenstein, E. *Macromolecules* **2001**, *34*, 3587. (h) Ishizone, T.; Tajima, H.; Torimae, H.; Nakahama, S. *Macromol. Chem. Phys.*, in press.

(18) Anderson, B. C.; Andrews, G. D.; Arthur, Jr., P.; Jacobson, H. W.; Melby, L. R.; Playtis, A. J.; Sharkey, W. H. *Macromolecules* **1981**, *14*, 1599.

(19) The observed M_n value increased with increasing the monomer-to-initiator ratio, while apparent deviation in M_n value was observed (Table 1, run 7). This is probably due to the trace amount of impurity in the monomer, resulting in the partial loss of initiator at the initial stage of polymerization.

(20) Varshney, S. K.; Jacobs, C.; Hautekeer, J. P.; Bayard, P.; Jérôme, R.; Fayt, R.; Teyssié, Ph. *Macromolecules* **1991**, *24*, 4997.

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

MA021257F