8312 *Macromolecules* **2003,** *36,* 8312−8319

Synthesis of Thermally Sensitive Water-Soluble Polymethacrylates by Living Anionic Polymerizations of Oligo(ethylene glycol) Methyl Ether Methacrylates

Seok Han, Mamoru Hagiwara, and Takashi Ishizone*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-852, Japan

Received June 11, 2003; Revised Manuscript Received August 20, 2003

ABSTRACT: Anionic polymerizations of 2-methoxyethyl methacrylate (**1**), 2-(2-methoxyethoxy)ethyl methacrylate (**2**), and 2-[2-(2-methoxyethoxy)ethoxy]ethyl methacrylate (**3**) were carried out with 1,1-diphenyl-3-methylpentyllithium/lithium chloride and diphenylmethylpotassium/diethylzinc in THF at −78 °C for 2−4 h. The resulting polymers possessed the predicted molecular weights based on the molar ratios between monomers to initiators and the narrow molecular weight distributions ($M_w/M_n < 1.1$). The stability of the propagating chain ends of poly(**2**) and poly(**3**) was confirmed by the quantitative efficiency in the reversible sequential block copolymerizations between **2** and **3**. New block copolymers having well-defined chain structures, poly(**2**)-*block*-poly(**3**), poly(**3**)-*block*-poly(**2**), polystyrene-*block*-poly(**1**), polystyrene-*block*-poly(**2**), and polystyrene-*block*-poly(**3**), were anionically synthesized. Both the solubility and the cloud point of polymers strongly depended on the length of hydrophilic oligo(ethylene glycol) unit. Poly(**2**) and poly(**3**) with longer oligo(ethylene glycol) chains were readily soluble in water, whereas poly(**1**) was insoluble in water. The aqueous solutions of poly(**2**) and poly(**3**) showed the reversible cloud points at 26 and 52 °C, respectively.

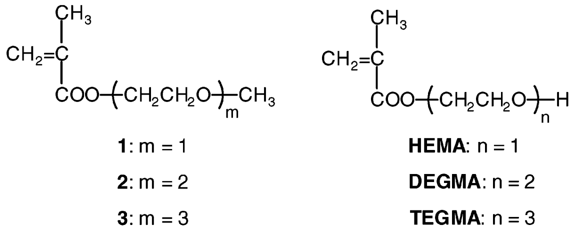
Introduction

Water-soluble polymers have attracted a great deal of attention over the years for industrial applications such as dispersants, stabilizers, emulsifiers, and flocculants.[1] The representative synthetic examples include poly(ethylene glycol) and poly(vinyl alcohol); several derivatives of poly(meth)acrylate,[2−6] poly(meth)acrylamide,[7,8] and poly(vinyl ether)[9] also show solubility in water by introducing nonionizable hydrophilic moieties on the side chains. Although various water-soluble polymers have been synthesized and studied by many research groups, the primary chain structures of polymers are not precisely controlled in most cases because of chain termination during the polymerization processes.

Among the water-soluble polymers listed above, polymethacrylates can be widely designed to provide water solubility by substituting suitable hydrophilic functionalities on the ester moieties.[2−6] Moreover, recent progress in the controlled polymerizations of methacrylates has enabled the synthesis of water-soluble polymethacrylates with precisely controlled chain structures such as predicted molecular weight, narrow molecular weight distribution, and sometimes high stereoregularity. For instance, tailored water-soluble polymethacrylates bearing 2,3-dihydroxypropyl[2] and 2-(*N*,*N*-dialkylamino)ethyl groups[3] and glucose functionality[4] are prepared via various synthetic routes.

Recently, we have succeeded in the tailored synthesis of new water-soluble polymethacrylate, poly[di(ethylene glycol) methacrylate], poly(DEGMA), and poly[tri(ethylene glycol) methacrylate], poly(TEGMA), via the living anionic polymerizations of 2-[2-[(*tert*-butyldimethylsilyl)oxy]ethoxy]ethyl methacrylate (DEGMA-Si) or 2-[2-[2-[(*tert*-butyldimethylsilyl)oxy]ethoxy]ethoxy]ethyl methacrylate (TEGMA-Si) followed by deprotection of the trialkylsilyl protecting groups.[10] Homopolymers and block copolymers with predicted molecular weights and narrow molecular weight distributions ($M_w/M_n = 1.1$) were obtained quantitatively. More importantly, the resulting poly(DEGMA) and poly(TEGMA) showed excellent solubility in water at any temperature, although the corresponding polymethacrylate ester of ethylene glycol, poly(2-hydroxyethyl methacrylate), poly(HEMA), was not soluble in water.[11,12] Therefore, introduction of longer oligo(ethylene glycol) units to the pendant ester moiety is very effective at solubilizing polymethacrylate in water. However, both protection of acidic OH functionality prior to the anionic polymerization and deprotection of trialkylsilyl groups after the polymerization are required to obtain water-soluble poly(DEGMA) and poly(TEGMA) via the above procedure.

Chart 1



In this study, we focus on the anionic polymerizations of a series of oligo(ethylene glycol) methyl ether methacrylates, MOEGMA, 2-methoxyethyl methacrylate (**1**), 2-(methoxyethoxy)ethyl methacrylate (**2**), and 2-[2-(methoxyethoxy)ethoxy]ethyl methacrylate (**3**) (Chart 1). These monomers are the counterparts of HEMA, DEGMA, and TEGMA, respectively, of which terminal OH functionalities on the side chains are masked with stable methoxy groups. Since only ether linkages are present in these methacrylates, direct anionic polymerizations of **1**−**3** should be possible. We expect the water solubility of poly(MOEGMA)s to be strongly dependent upon the side chain lengths of oligo(ethylene glycol) units similar to the cases of poly[oligo(ethylene glycol) methacrylate]s,

10.1021/ma0347971 CCC: $25.00

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

run	monomer type, mmol	initiator type, mmol	additive type, mmol	time, h	$M_n \times 10^{-3}$		M_w/M_n[d]	tacticity (%)[e]		
					calcd[b]	obsd[c]		*mm*	*mr*	*rr*
1	**1**, 9.59	*s*-BuLi, 0.0524/DPE,[f] 0.105		2	27	37	1.16	3	32	65
2	**1**, 8.78	*s*-BuLi, 0.0813/DPE, 0.115	LiCl, 0.505	2	16	16	1.03	4	30	66
3	**1**, 9.18	Ph_2CHK,[g] 0.112		2	12	12	1.28	17	52	31
4	**1**, 9.19	Ph_2CHK, 0.104	Et_2Zn, 1.75	2	13	14	1.04	13	52	35
5	**2**, 4.88	*s*-BuLi, 0.0644/DPE, 0.217		2	14	14	1.33	6	29	65
6	**2**, 5.25	Ph_2CHLi,[h] 0.101	LiCl, 0.489	2	10	13	1.04	4	23	73
7	**2**, 5.14	*s*-BuLi, 0.195/DPE, 0.362	LiCl, 1.59	2	5.2	5.5	1.06	5	30	65
8	**2**, 6.29	*s*-BuLi, 0.0907/DPE, 0.312	LiCl, 0.466	2	13	13	1.05	4	26	70
9	**2**, 7.37	*s*-BuLi, 0.0735/DPE, 0.258	LiCl, 0.390	2	19	21	1.04			
10	**2**, 5.03	*s*-BuLi, 0.0328/DPE, 0.0841	LiCl, 0.234	3	29	37	1.08	3	25	72
11	**2**, 6.66	Ph_2CHK, 0.124		2	10	10	1.24	19	48	33
12	**2**, 5.93	Ph_2CHK, 0.0702	Et_2Zn, 1.48	2	16	17	1.09	18	48	34
13	**2**, 5.01	Ph_2CHK, 0.0384	Et_2Zn, 0.455	3	25	27	1.04	14	44	42
14	**3**, 1.71	*s*-BuLi, 0.0434/DPE, 0.324		3	9.4	14	1.42	5	26	69
15	**3**, 3.62	*s*-BuLi, 0.0750/DPE, 0.262	LiCl, 0.406	3	11	16	1.09	4	24	72
16	**3**, 2.11	Ph_2CHK, 0.0557		4	9.0	11	1.47	6	34	60
17	**3**, 2.59	Ph_2CHK, 0.105	Et_2Zn, 1.70	3	5.9	6.7	1.09	3	41	56
18	**3**, 3.21	Ph_2CHK, 0.0918	Et_2Zn, 1.34	3	8.3	7.0	1.11	5	39	56
19	**3**, 3.38	Ph_2CHK, 0.0547	Et_2Zn, 1.33	4	15	16	1.05	4	36	60
20	**3**, 3.90	Ph_2CHK, 0.0305	Et_2Zn, 1.43	4	30	37	1.03	3	36	61

[a] Yield ~ 100%. [b] M_n(calcd) = (MW of monomer) × [M]/[I] + MW of initiator. [c] M_n(obsd) was determined by end-group analysis using ^{1}H NMR. [d] M_w/M_n was determined by SEC calibration using PMMA standards in THF. [e] The triad tacticity was determined by the ^{1}H NMR signal intensity of α-methyl proton (*mm* = 1.25 ppm, *mr* = 1.05 ppm, and *rr* = 0.90 ppm) of polymers. [f] 1,1-Diphenylethylene. [g] Diphenylmethylpotassium. [h] Diphenylmethyllithium.

poly(OEGMA). Although the syntheses of polymers of MOEGMA have been reported by several researchers,[5,6] the employed monomers are usually mixtures of oligo(ethylene glycol) alkyl ethers with a distribution of side chain lengths. Furthermore, the primary chain structures of the obtained poly(MOEGMA)s are not precisely controlled,[13] since they have been generally prepared using conventional free-radical polymerizations. We herein polymerize **1**−**3** anionically to synthesize the (co)polymers with well-defined chain structures. The purpose of this study is to clarify the effects of the terminal structure of the side chain, side chain lengths, and the molecular weight parameters on the water solubilities and to demonstrate thermally sensitive solubility of poly(**2**) and poly(**3**) in water.

Results and Discussion

Anionic Polymerization of 1−3. Monomer **3** was synthesized by reaction of methacryloyl chloride with tri(ethylene glycol) methyl ether in the presence of triethylamine in diethyl ether, while **1** and **2** were commercially available. All the monomers were thoroughly purified by column chromatography and fractional distillation prior to their polymerizations.

The anionic polymerizations of **1**−**3** were carried out in THF at −78 °C for 2−4 h with either 1,1-diphenyl-3-methylpentyllithium (DMPLi), an adduct of *s*-BuLi and 1,1-diphenylethylene, diphenylmethyllithium (Ph_2CHLi), or diphenylmethylpotassium (Ph_2CHK) as the initiator in the absence and in the presence of LiCl[14] and Et_2Zn.[15] When a THF solution of monomer was added to the initiator solution, the red color of the initiator rapidly disappeared to give a colorless solution. All of the polymerizations of **1**−**3** proceeded homogeneously in THF at −78 °C. After quenching the polymerization with degassed methanol, the conversion of monomer was estimated by ^{1}H NMR spectroscopy. Polymer was obtained quantitatively after precipitating the polymerization system into a large excess of hexane. The molecular weights of poly(**1**−**3**)s were determined by end-group analysis using the signal intensity between the aromatic proton of the initiator residue (7.21−7.23 ppm) and the proton derived from the repeating units (4.11 ppm) as previously reported.[16] The results of anionic homopolymerization of **1**−**3** are summarized in Table 1.

The polymerizations of **1**−**3** quantitatively proceeded with DMPLi in THF at −78 °C within 2−3 h. The resulting polymers were characterized by size exclusion chromatography (SEC). The SEC curves of polymers obtained with DMPLi showed unimodal, but rather broad, molecular weight distributions, and the polydispersity indices, M_w/M_n, were 1.16−1.42. The M_n values of poly(**1**) and poly(**3**), determined by ^{1}H NMR spectroscopy, were higher than the calculated values based on the molar ratios of monomers to initiator, while poly(**2**) had the controlled molecular weight. In contrast, poly(**1**−**3**)s with very narrow molecular weight distributions (M_w/M_n < 1.1) were always produced in quantitative yields at −78 °C within 3 h, when 4−8-fold excess of LiCl to DMPLi was added. The observed M_ns of polymers agreed well with the predicted ones from the molar ratios between monomers and initiator.[17] A binary initiator system of Ph_2CHLi and LiCl also afforded the poly(**2**) having well-defined chain structures (Table 1, run 6). A similar additive effect of LiCl on narrowing of molecular weight distributions has been previously reported in the anionic polymerizations of various (meth)acrylate monomers.[12,14,18] The reported explanation for the additive effect of LiCl involves the reduction of polymerization rate, the lowered nucleophilicity of the propagating chain end, and the equilibrium shift from the ionic associated state toward the nonassociated species in the presence of a common-ion salt.[19]

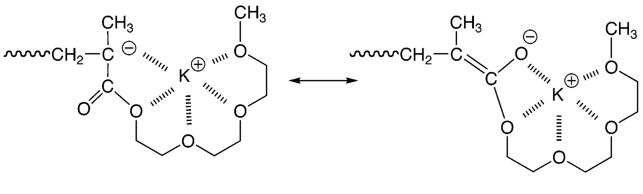
We then attempted to polymerize **1**−**3** with an organopotassium initiator, Ph_2CHK, under similar reaction conditions. Complete conversions of **1**−**3** were always attained with Ph_2CHK in THF at −78 °C within 4 h. Although the poly(**1**−**3**)s produced with Ph_2CHK had the predicted molecular weights, their molecular weight distributions were rather broad (M_w/M_n = 1.24−1.47). A binary initiator system of Ph_2CHK/Et_2Zn effectively narrowed the molecular weight distributions of poly(**1**−**3**)s. The M_w/M_n values were indeed reduced to

Table 2. Anionic Block Copolymerization of 1−3 in THF at −78 °C[a]

				block copolymer (homopolymer[b])		
				$10^{-3}M_n$		
run	initiator	first monomer [M1]/[initiator]	second monomer [M2]/[initiator]	calcd	obsd[c]	M_w/M_n
21	*s*-BuLi	styrene, 121[d]	**1**, 84.5	25	24	1.05
22	*s*-BuLi	styrene, 49.9[d]	**2**, 57.3	16	16	1.07
23	*s*-BuLi	styrene, 41.5[d]	**3**, 36.0	13	15	1.05
24	Ph_2CHK[e]	**2**, 34.7	**3**, 35.9	15 (6.7)	15 (6.4)	1.04 (1.04)
25	Ph_2CHK[e]	**3**, 27.4	**2**, 48.4	16 (6.5)	17 (6.2)	1.06 (1.05)

[a] Yield ~ 100%. Polymerization time: 3 h for **1**−**3**; 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 ^1H NMR. [d] A 2-fold excess of 1,1-diphenylethylene and 15-fold excess of Et_2Zn were added to the living anionic polystyrene before the addition of second monomer. [e] A 15-fold excess of Et_2Zn was added to Ph_2CHK before the polymerization of first monomer.

Scheme 1



around 1.1. Thus, **1**−**3** quantitatively underwent the anionic polymerizations with Ph_2CHK in the presence of Lewis acidic Et_2Zn to afford the polymers with the tailored molecular weights and the narrow molecular weight distributions. The polymerization behaviors of **1**−**3** are good accordance with our previous polymerization results of various (meth)acrylate monomers,[20] including trialkylsilyl-protected OEGMAs, DEGMA-Si, and TEGMA-Si.[10] We now consider that the added Et_2Zn as a weak Lewis acid effectively reduces both the polymerization rate and the nucleophilicity by interacting with the propagating enolate anions to result in the narrowing of molecular weight distribution.[10,15,20]

The stereoregularity of the polymers was estimated by the relative signal intensity of α-methyl protons appearing at 0.90−1.25 ppm in the ^1H NMR spectra. The triad tacticities are shown in Table 1. The poly(**1**−**3**)s produced with organolithium initiators in THF always possessed syndiotactic configurations regardless of the lengths of oligo(ethylene glycol) units. This is consistent with the previous reports observed in the polymerizations of most of methacrylates under the similar conditions (with organolithiums in THF at −78 °C).[14,18] Addition of LiCl to the initiator did not affect the stereoregularity of the resulting polymers. In contrast, the poly(**1**) obtained with either Ph_2CHK or Ph_2CHK/Et_2Zn had *mr*-rich configurations. No significant additive effect of Et_2Zn on the stereoregularity of poly(**1**) was observed, as was previously observed in the polymerization of other methacrylates.[15,20] The *mr* contents decreased and the *rr* contents alternatively increased with increasing lengths of oligo(ethylene glycol) units. The poly(**3**)s bearing a tri(ethylene glycol) moiety possessed *rr*-rich configurations, even when the polymerizations were carried out with either Ph_2CHK or Ph_2CHK/Et_2Zn, whereas the stereoregularities were still *mr*-rich in the cases of poly(**2**)s. The plausible explanation for this polymerization behavior is that an association of the multidentate oligo(ethylene glycol) methyl ether moiety occurs with potassium ion at the propagating chain ends (Scheme 1), as proposed for glymes. The longer units of **3** would form stronger and bulkier propagating species at the terminal to change the tacticity of poly(**3**) compared with those of poly(**1**) and poly(**2**). We have previously observed that the anionic polymerizations of DEGMA-Si and TEGMA-Si afforded the *mr*-rich polymers under similar conditions using organopotassium initiators.[10] In the cases of *tert*-butyldimethylsilyl-protected OEGMAs, the lengths of oligo(ethylene glycol) units did not affect the stereoregularities of the resulting polymers. The bulky *tert*-butyldimethylsilyl groups at the side chain might suppress association of oligo(ethylene glycol) chains with the counterion at the propagating chain ends. Thus, the stereoregularities of poly(**3**) are always predominantly *rr*-rich regardless of the counterion of initiators, while the counterions dominate the stereoregularity of poly(**1**) and poly(**2**).

Block Copolymerization of 1−3. The successful anionic polymerizations of **1**−**3** in the preceding section prompted us to synthesize tailored block copolymers containing poly(**1**−**3**) segments. The results of sequential copolymerization of **1**−**3** are shown in Table 2. At first, the sequential block copolymerizations of **1**−**3** with styrene were performed to synthesize amphiphilic block copolymers with well-defined chain structures. Living anionic polystyrene was synthesized with *s*-BuLi in THF at −78 °C for 10 min. THF solutions of 1,1-diphenylethylene (DPE) and Et_2Zn were successively added to the living polystyrene to decrease the nucleophilicity of the anionic species. The resulting DPE-capped living polystyrene was then employed as the macroinitiator for **1**−**3** in the presence of Et_2Zn. After the addition of monomers **1**−**3** to the polymerization systems, the copolymers were obtained in quantitative yields. All the resulting copolymers had unimodal and narrow molecular weight distributions in the SEC curves. The compositions of copolymers estimated from ^1H NMR agreed with the feed molar ratios of **1**−**3** and styrene. In addition, the observed molecular weights were in accordance with the values calculated from the monomer-to-initiator ratios. These characterization results demonstrate that a series of tailored diblock copolymers of styrene and **1**−**3**, polystyrene-*block*-poly(**1**), polystyrene-*block*-poly(**2**), and polystyrene-*block*-poly(**3**), are successfully synthesized via the sequential copolymerizations. In addition to the well-defined chain architectures, the resulting copolymers are amphiphilic due to the water-soluble poly(**2**) and poly(**3**) segments and the hydrophobic polystyrenes.

We next attempted to polymerize **2** and **3** to synthesize block copolymers showing water solubility. The first-stage polymerization of **2** was initiated with Ph_2CHK/Et_2Zn in THF at −78 °C for 2 h. After the complete consumption of **2**, a small portion of the polymerization system was isolated to characterize the homopolymer of **2**. A THF solution of the second monomer **3** was added to the residue of polymerization system and polymerized

Table 3. Solubility of Polymers (I = Insoluble; S = Soluble)

solvent	poly(**1**)	poly(**2**)	poly(**3**)	poly(**2**)-*b*-poly(**3**)	poly(HEMA)[a]	poly(DEGMA)[b]	poly(TEGMA)[c]	poly(MMA)[d]
hexane	I	I	I	I	I	I	I	I
benzene	S	S	S	S	I	I	I	S
CHCl$_3$	S	S	S	S	I	S	S	S
acetone	S	S	S	S	I	I	S	S
ethyl acetate	S	S	S	S	I	I	S	S
Et$_2$O	I	I	I	I	I	I	I	I
1,4-dioxane	S	S	S	S	I	S	S	S
THF	S	S	S	S	I	I	I	S
DMF	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S
EtOH	I	S	S	S	S	S	S	I
MeOH	I	S	S	S	S	S	S	I
water	I	S[e]	S[f]	S[g]	I	S	S	I

[a] Poly(2-hydroxyethyl methacrylate). [b] Poly[di(ethylene glycol) methacrylate]. [c] Poly[tri(ethylene glycol) methacrylate]. [d] Poly(methyl methacrylate). [e] Cloud point around 26 °C. [f] Cloud point around 52 °C. [g] Cloud point around 39 °C.

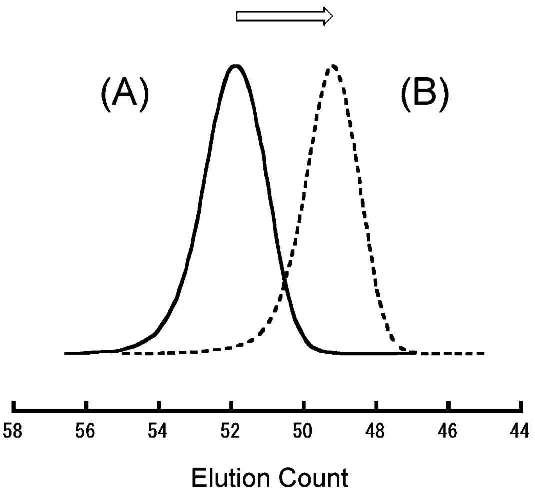


Figure 1. SEC curves of poly(**2**) (peak A, $M_n = 6400$, $M_w/M_n = 1.04$) and poly(**2**)-*block*-poly(**3**) (peak B, $M_n = 15\,000$, $M_w/M_n = 1.04$) measured in THF.

further for 3 h at −78 °C. A homopoly(**2**) and a copolymer were obtained in quantitative yields after termination with methanol. The SEC curve of the resultant copolymer shifts toward the higher molecular weight region from that of homopoly(**2**) with maintaining the unimodal and narrow shape, as shown in Figure 1. ^{1}H NMR analysis revealed that the copolymer had the predicted composition and controlled molecular weights, which were based on the molar ratios of comonomers and initiator. In a similar manner, reversed sequential addition of **3** (first monomer) and **2** (second monomer) quantitatively gave a block copolymer, poly(**3**)-*block*-poly(**2**), with well-defined structures, as shown in Table 2. These confirm that the resulting propagating carbanions of poly(**2**) and poly(**3**) are sufficiently stable to initiate the second-stage polymerizations in quantitative efficiencies. Thus, the living character of the anionic polymerizations of polar functional methacrylate monomers, **2** and **3**, enables the synthesis of novel tailored block copolymers showing water solubility, as shown below.

Solubility of Polymers. The poly(MOEGMA)s, poly(**1**), poly(**2**), and poly(**3**), obtained in this study are the counterparts of poly(HEMA),[11,12] poly(DEGMA),[10] and poly(TEGMA),[10] respectively, as pointed out in the Introduction. Solubilities of these polymers are shown in Table 3, with that of poly(MMA) as the reference. Poly(**1**−**3**)s were insoluble in hexane and diethyl ether but showed good solubility in a wide range of organic solvents. Interestingly, poly(**2**) and poly(**3**) were soluble in water, methanol, and ethanol, while poly(**1**) did not dissolve in these highly polar solvents. The poly(**2**)-*block*-poly(**3**) obtained in the preceding section also showed water solubility, as expected. Longer oligo(ethylene glycol) units apparently increased the polarities of polymers to afford the solubility in the polar protoic solvents, as expected. The effect of terminal OH group in the pendant oligo(ethylene glycol) moieties is evident in the difference of solubilities between poly(OEGMA)s and the corresponding methyl ethers, poly(MOEGMA). Masking of polar OH functionalities of poly(OEGMA)s with methyl groups provided a wide solubility of poly(MOEGMA)s in solvents such as benzene, acetone, and ethyl acetate, while all the poly(OEGMA)s were insoluble in these solvents. The higher polarity of poly(OEGMA) is clear from the solubility of poly(HEMA) in methanol and ethanol, although the corresponding methyl ether, poly(**1**), was insoluble. Thus, we have successfully found the water solubility of poly(MOEGMA)s by tuning the lengths of oligo(ethylene glycol) side chains, as is previously attained in the molecular design of poly(OEGMA)s.[10]

Cloud Point of Polymers in Water. Among the water-soluble polymers, several polymers exhibit a temperature-dependent solubility in water with a lower critical solution temperature (LCST). The typical examples include poly(ethylene glycol), poly(2-(dimethylamino)ethyl methacrylate),[3] poly(*N*-substituted acrylamide)s,[7,8] and poly(vinyl ether)s.[9] The aqueous solutions of these polymers show the cloud points on either the heating or cooling procedure. For example, thermally induced phase separation behaviors of cationically synthesized poly(vinyl ether)s bearing oligo(ethylene glycol) units have been reported by Aoshima and coworkers.[9] The cloud points of these polymers are strongly dependent on the lengths of oligo(ethylene glycol) moieties, as expected.

We herein found the thermally limited solubility of poly(**2**) and poly(**3**) in water. The aqueous solution of poly(**2**) was transparent at 20 °C, but it suddenly became cloudy around 26 °C during the course of heating. Some precipitate was finally observed in the milky solution, when the polymer solution was further heated. In a similar manner, poly(**3**)s also exhibited the cloud points in water around 52 °C. The higher cloud point of poly(**3**) strongly indicates its higher water solubility compared with that of poly(**2**) with shorter oligo(ethylene glycol) unit. The lengths of oligo(ethylene glycol) moieties certainly affect not only the solubility in water but also the cloud points of poly(MOEGMA)s.

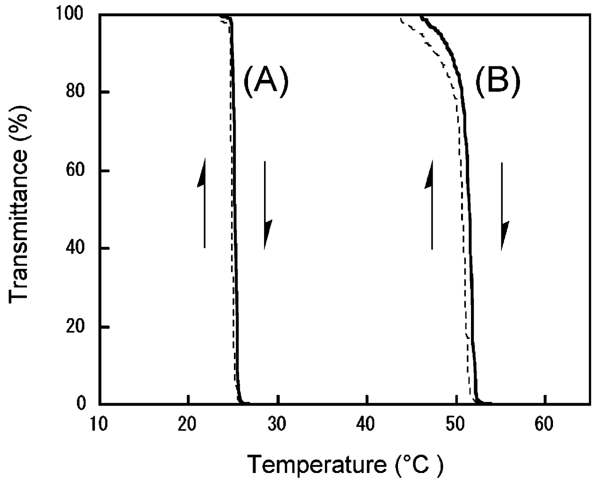


Figure 2. Transmittance vs temperature curves (500 nm, 0.3 °C/min; solid line: heating; dotted line: cooling) obtained for 0.2 wt % solutions of poly(**2**) (curve A, $M_n = 17\,000$, $M_w/M_n = 1.09$) and poly(**3**) (curve B, $M_n = 16\,000$, $M_w/M_n = 1.05$) in water.

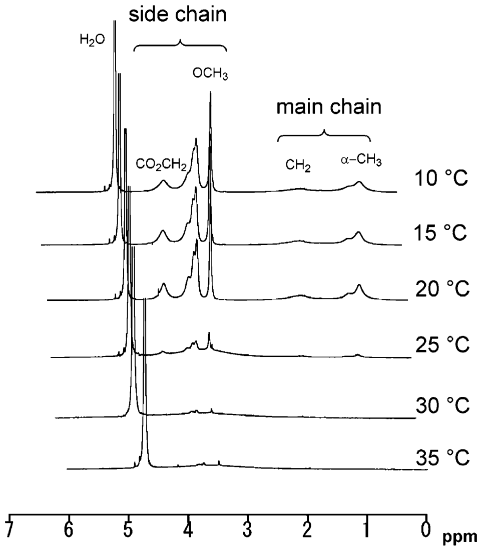


Figure 3. ^{1}H NMR spectra of poly(**2**) ($M_n = 37\,000$, $M_w/M_n = 1.08$) at various temperatures in D_2O.

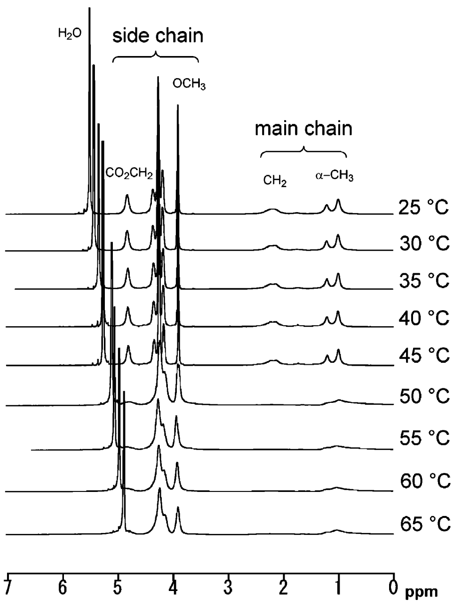


Figure 4. ^{1}H NMR spectra of poly(**3**) ($M_n = 16\,000$, $M_w/M_n = 1.05$) at various temperatures in D_2O.

Figure 2 shows the phase diagrams for the aqueous solutions of poly(**2**) and poly(**3**) by monitoring their transmittances. The phase separation of aqueous solution of poly(**2**) occurred fairly sensitively, while the poly(**3**) exhibits rather slow phase separation. The process of each polymer was actually reversible, but small hysteresis on temperature ($\Delta T = 1$ °C) was observed on a heating and a cooling cycle (±0.3 °C min^{-1}). An aqueous solution of poly(**2**)-*block*-poly(**3**) showed the cloud point around 39 °C, which was intermediate between those of poly(**2**) and poly(**3**).

The behavior of phase separation can be also monitored by ^{1}H NMR measurement of polymer solutions in D_2O. Figures 3 and 4 show the ^{1}H NMR spectra of aqueous solutions (0.2 wt %) of poly(**2**) and poly(**3**) on the heating processes, respectively. At 15 and 20 °C, the proton signals of poly(**2**) were clearly observed, indicating the mobility of the side chain and the polymer main chain. However, on heating the polymer solution toward 25 °C, all the proton signals suddenly became broader and almost disappeared over 30 °C. This ^{1}H NMR observation again supports that the phase separation of poly(**2**) occurs around 25 °C with suppressing the movements of polymer structure. In the case of poly(**3**), the broadening of ^{1}H NMR spectra was similarly ascertained between 45 and 50 °C, as expected from the optical observation. In fact, the proton signals of α-CH_3, CH_2 of polymer main chain, and $COOCH_2$ moiety showed the significant broadening around 50 °C, meaning their restricted movements along and close to the hydrophobic polymer chain. By contrast, the proton signals of flexible and hydrophilic side chain were somehow observed even at the elevated temperatures. The oligo(ethylene glycol) unit of poly(**3**) longer than poly(**2**) seemed to maintain the movements to some extent even in the precipitated solution, although the phase separation took place over the LCST at 52 °C. No significant change in the ^{1}H NMR spectra of poly(DEGMA) and poly(TEGMA) was ascertained between 10 and 70 °C in D_2O.[10] All of the proton signals became rather narrower on heating due to the accelerated mobility as usual, supporting the excellent and thermally independent water solubility of both polymers. The terminal OH groups on the side chains of poly(DEGMA) and poly(TEGMA) play a very important role to inhibit the phase separation accompanied by the dehydration.

To investigate the effect of molecular weights on the cloud points, a series of well-defined poly(**2**) and poly(**3**) were employed. In each case, the molecular weight distribution was very narrow ($M_w/M_n < 1.1$) and the tacticity was predominantly *rr*-rich. Figures 5 and 6 show the relationship between the cloud point and the molecular weight of poly(**2**) and poly(**3**), respectively. In the both cases, the cloud points tended to decrease with increasing the M_n values of polymers. In addition, the polymer samples having higher molecular weights tended to show a sharp response in transmittance. These suggest that the longer polymer chain easily forms the intermolecular and/or intramolecular aggregation at lower temperature, which results in the quick phase separation. This is consistent with the previous observation for the cationically synthesized poly(vinyl ether)s bearing oligo(ethylene glycol) units.[9]

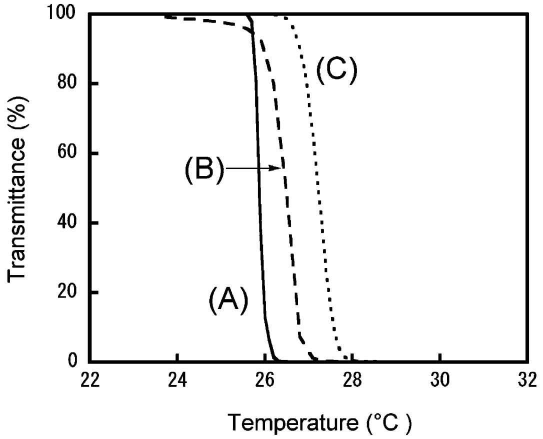


Figure 5. Transmittance vs temperature curves (500 nm, 0.3 °C/min) obtained for 0.2 wt % aqueous solution of poly(**2**)s synthesized with DMPLi/LiCl. (curve A, M_n = 37 000, M_w/M_n = 1.08; curve B, M_n = 21 000, M_w/M_n = 1.04; curve C, M_n = 13 000, M_w/M_n = 1.05).

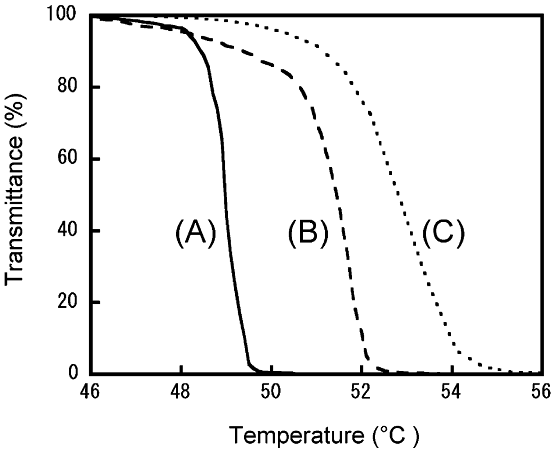


Figure 6. Transmittance vs temperature curves (500 nm, 0.3 °C/min) obtained for 0.2 wt % aqueous solution of poly(**3**)s synthesized with Ph_2CHK/Et_2Zn (curve A, M_n = 37 000, M_w/M_n = 1.03; curve B, M_n = 16 000, M_w/M_n = 1.05; curve C, M_n = 6700, M_w/M_n = 1.09).

The effect of stereoregularity on the cloud point was examined in three poly(**2**) samples synthesized with DMPLi/LiCl (Table 1, run 8), $Ph_2CHLi/LiCl$ (Table 1, run 6), or Ph_2CHK/Et_2Zn (Table 1, run 13). All of the polymers have comparable molecular weights and narrow molecular weight distributions, although the stereoregularity of the polymers was influenced by the counterions of the employed initiators. The polymer having *mr*-rich configuration (run 13) showed the cloud point at 25 °C, while the cloud points of *rr*-rich polymers (runs 6 and 8) were slightly higher around 27 °C. This small difference in cloud point can be explained by the effect of stereoregularity of poly(**2**). On the other hand, since all the poly(**3**) samples had *rr*-rich configuration, we could not discuss the effect of tacticity on the cloud point. Poly(**2**) and poly(**3**), poly(MOEGMA)s, are the novel thermally responsible polymers showing cloud points in water around either 26 or 52 °C.

Glass Transition Temperature of Polymers. Poly(**2**) and poly(**3**) obtained in this study were colorless, sticky solids, whereas poly(**1**) was a white powder just after freeze-drying. They were extremely hygroscopic, and even the powdery poly(**1**) became a sticky solid after standing in air. The glass transition temperatures (T_gs) of polymers were measured by differential scanning calorimetry (DSC). The T_g values of poly(**1**), poly(**2**), and poly(**3**) were 30, −40, and −47 °C, respectively. The longer flexible oligo(ethylene glycol) side chains of poly(**2**) and poly(**3**) drastically decreased the T_g values compared to that of poly(**1**). A similar effect of side chain length on T_g change has been observed for a series of poly(OEGMA)s.[10] Poly(DEGMA) and poly(TEGMA) had low T_gs at −95 and −130 °C, respectively,[10] while the reported T_g values of poly(HEMA)s were widely distributed between 38 and 120 °C probably due to their stereoregularity.[21]

In conclusion, we have succeeded in the living anionic polymerizations of methoxy-capped oligo(ethylene glycol) methacrylates, **1**−**3**, to give the polymers with controlled molecular weights and narrow molecular weight distributions. The resulting poly(**2**) and poly(**3**) were soluble in water, and their aqueous solutions showed typical reversible cloud points at 26 and 52 °C, respectively.

Experimental Section

Materials. Monomers **1** (Aldrich, 99%) and **2** (Nippon Oil Fat, 99%) were purified by column chromatography (silica gel, hexane/ethyl acetate), followed by fractional distillation from CaH_2 in vacuo. Commercially available methacryloyl chloride (Tokyo Kasei, <90%) was used without purification. Tri(ethylene glycol) monomethyl ether (Aldrich, 95%) was dried and distilled over CaH_2 under reduced pressure. Triethylamine (Aldrich, 99%) was 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 (Aldrich, 99%) 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. 1,1-Diphenylethylene (Tokyo Kasei, <98%) 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 from $LiAlH_4$ 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. Ph_2CHLi and Ph_2CHK were prepared by the reaction of metal naphthalenides with a 1.1-fold excess of diphenylmethane in THF at room temperature for 48 h.[22] The concentrations of initiators were determined by colorimetric titration using standardized 1-octanol in THF in a sealed reactor in vacuo as previously reported.[23]

Measurements. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX300 (300 MHz for ^1H and 75 MHz for ^{13}C) in $CDCl_3$, D_2O, or d_6-DMSO. Tacticity of polymers was determined by the ^1H NMR integral ratio of three split α-methyl proton signals appearing at 0.90−1.25 ppm similar to the previous report of poly(methyl methacrylate).[24] Three signals were assigned as *mm* (1.25 ppm), *mr* (1.05 ppm), and *rr* (0.90 ppm) triads. Infrared spectra (KBr disk or neat) were recorded on a JASCO FT/IR-460Plus instrument. 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 three polystyrene gel columns (TOSOH G5000H_{XL}, G4000H_{XL}, and G3000H_{XL}, measurable molecular weight range 2×10^3−4×10^6) and with ultraviolet (254 nm) or refractive index detection. 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}. The cloud points of poly(**2**) and poly(**3**) in water were determined by monitoring the transmittance using a JASCO UVIDEC-660 spectrometer. Transmittance of 0.2 wt % of polymer solution at 500 nm was monitored in a PMMA cell (path length of 1.0 cm) at either a heating or a cooling rate of 0.3 °C min^{-1}.

2-[2-(2-Methoxyethoxy)ethoxy]ethyl Methacrylate (3). A solution of methacryloyl chloride (7.16 g, 49.7 mmol) in ether (20 mL) was added dropwise to a mixture of tri(ethylene glycol) monomethyl ether (13.5 g, 75.9 mmol), triethylamine (14.5 g, 143 mmol), and diethyl ether (60 mL) with stirring at 0 °C under nitrogen. The reaction mixture was stirred overnight at room temperature and filtered to remove precipitated triethylamine hydrochloride. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 10/1−10/4). Vacuum distillation in the presence of a trace amount of methylene blue gave a colorless liquid of **3** (4.36 g, 18.8 mmol, 27%, bp 90−95 °C/0.4 mmHg).

^{1}H NMR (CDCl$_3$): δ 1.94 (s, 3H, α-CH_3), 3.37 (s, 3H, OCH$_3$), 3.55 (t, J = 4.8 Hz, 2H, CH_2OCH$_3$), 3.69 (m, 6H, OCH$_2$CH$_2$OCH_2CH_2OCH_2CH$_2$OCH$_3$), 3.74 (t, J = 4.8 Hz, 2H, COOCH$_2$CH_2), 4.29 (t, J = 4.8 Hz, 2H, COOCH_2), 5.57 and 6.12 (2s, 2H, CH_2=). ^{13}C NMR (CDCl$_3$): δ 18.4 (α-CH$_3$), 59.1 (OCH$_3$), 64.0 (COOCH$_2$), 69.2 (COOCH$_2$$CH_2$O), 70.7 (COOCH$_2CH_2OCH_2$$CH_2OCH_2CH_2OCH_3$), 72.0 (CH$_2$$CH_2OCH_3$), 125.8 ($CH_2$=), 136.2 (CH$_2$=$C$), 167.4 ($C$=O). IR (neat, cm^{-1}): 943, 1040, 1112, 1170, 1296, 1321, 1454, 1639, 1719 (C=O), 2700−3000. Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.90; H, 8.62. Found: C, 57.00; H, 8.41.

Purification of Monomers. After careful fractional distillation, monomers were degassed and sealed off in an apparatus equipped with a break-seal in the presence of CaH$_2$ and diluted with dry heptane. The monomer solution in heptane was stirred for 20 h at room temperature and distilled from 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.[23] A typical polymerization procedure was as follows: A THF solution (3.91 mL) of 1,1-diphenylethylene (0.0800 M, 0.312 mmol) was added to a heptane solution (2.10 mL) of *s*-BuLi (0.0432 M, 0.0907 mmol) through the break-seal at −78 °C. After 20 min, LiCl (0.0643 M, 0.466 mmol) in THF (7.25 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** (1.18 g, 0.585 M, 6.29 mmol) in THF (10.75 mL) was added rapidly to the initiator system at −78 °C through the break-seal with vigorous shaking of the apparatus. After standing 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 hexane to precipitate poly(**2**) (1.18 g, 100%, M_n = 13 000, M_w/M_n = 1.05).

The resulting polymers were further purified by reprecipitations in a THF/hexane 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(1). ^{1}H NMR (CDCl$_3$): δ 0.8−1.3 (m, 3H, α-CH_3), 1.8−2.1 (br, 2H, CH_2), 3.40 (s, 3H, OCH$_3$), 3.62 (bs, 2H, COOCH$_2$CH_2OCH$_3$), 4.13 (bs, 2H, COOCH_2). ^{13}C NMR (CDCl$_3$): δ 16−20 (α-CH$_3$), 44−45 (main chain quarternary), 54 (main chain CH$_2$), 58.8 (OCH$_3$), 63.7 (COOCH$_2$), 69.9 (COOCH$_2$$CH_2$O), 178 ($C$=O). IR (KBr, cm^{-1}): 1030, 1128, 1156, 1244, 1271, 1453, 1729 (C=O), 2700−3000.

Poly(2). ^{1}H NMR (CDCl$_3$): δ 0.8−1.3 (m, 3H, α-CH_3), 1.7−2.1 (br, 2H, CH_2), 3.40 (s, 3H, OCH$_3$), 3.56 (bs, 2H, CH_2OCH$_3$), 3.63 (bs, 2H, OCH_2CH$_2$OCH$_3$), 3.68 (bs, 2H, COOCH$_2$CH_2), 4.11 (bs, 2H, COOCH_2). ^{13}C NMR (CDCl$_3$): δ 16−20 (α-CH$_3$), 44−45 (main chain quarternary), 54 (main chain CH$_2$), 59.1 (OCH$_3$), 64.0 (COOCH$_2$), 68.8 (COOCH$_2$$CH_2$O), 70.6 ($CH_2CH_2OCH_3$), 72.2 (CH$_2$$CH_2OCH_3$), 177 ($C$=O). IR (KBr, cm^{-1}): 1034, 1114, 1247, 1453, 1728 (C=O), 2700−3000.

Poly(3). ^{1}H NMR (CDCl$_3$): δ 0.8−1.2 (m, 3H, α-CH_3), 1.7−2.2 (br, 2H, CH_2), 4.00 (s, 3H, OCH$_3$), 3.56 (bs, 2H, CH_2OCH$_3$), 3.66 (m, 8H, COOCH$_2$CH_2OCH_2CH_2OCH_2CH$_2$OCH$_3$), 4.09 (bs, 2H, COOCH_2). ^{13}C NMR (CDCl$_3$): δ 16−20 (α-CH$_3$), 44−45 (main chain quarternary), 54 (main chain CH$_2$), 59.1 (OCH$_3$), 63.9 (COOCH$_2$), 68.5 (COOCH$_2$$CH_2$O), 70.6 (COOCH$_2CH_2OCH_2$$CH_2OCH_2CH_2OCH_3$), 72.0 (CH$_2$$CH_2OCH_3$), 177 ($C$=O). IR (KBr, cm^{-1}): 1033, 1113, 1248, 1454, 1729 (C=O), 2700−3000.

Block Copolymerization. Each block copolymerization was carried out in an all glass-apparatus equipped with break-seals under high-vacuum conditions similar to the homopolymerization. A typical procedure of sequential block copolymerization (Table 2, run 22) was as follows. Living anionic polystyrene was prepared by the reaction of styrene (0.41 g, 3.94 mmol) in THF (11.3 mL) with *s*-butyllithium (0.0484 M, 0.0789 mmol) in heptane (1.63 mL) at −78 °C for 30 min. Then, 1,1-diphenylethylene (0.0347 M, 0.181 mmol) in THF (5.22 mL) and Et$_2$Zn (0.356 M, 1.35 mmol) in THF (3.80 mL) were successively added to the resulting living polystyrene at −78 °C. A THF solution (10.8 mL) of **2** (0.85 g, 4.52 mmol) was finally added to the end-capped living polystyrene at −78 °C and reacted for 2 h to complete the polymerization of **2**. The polymerization was quenched with degassed methanol, and the reaction mixture was allowed to stand for 12 h to precipitate the zinc compounds. After filtration to remove the zinc compounds, the polymer solution was concentrated under reduced pressure. The residue was again dissolved in 10 mL of THF, and the THF solution was poured into hexane to precipitate the polymer. The polymer was purified by reprecipitations from THF solution into hexane twice and by freeze-drying from benzene solution. The yield of polymer was almost quantitative (1.26 g, ~ 100%, M_n = 16 000, M_w/M_n = 1.07). The resulting polymer was characterized by ^{1}H NMR and IR spectroscopies.

Acknowledgment. This research was partly supported by Grant-in Aid (14550833), from The Ministry of Education, Science, Sports, and Culture, Japan. T.I. appreciates the Shorai Foundation and Iwatani Foundation for their financial support.

References and Notes

(1) Bolto, B. *Prog. Polym. Sci.* **1995**, *20*, 1987.

(2) (a) Mori, H.; Hirao, A.; Nakahama, S. *Macromolecules* **1994**, *27*, 35. (b) Mori, H.; Hirao, A.; Nakahama, S.; Senshu, K. *Macromolecules* **1994**, *27*, 4093. (c) Hoogeveen, N. G.; Cohen Stuart, M. A.; Fleer, G. J.; Frank, W.; Arnold, M. *Macromol. Chem. Phys.* **1996**, *197*, 2553. (d) Zhang, H.; Ruckenstein, E. *Macromolecules* **2000**, *33*, 4738.

(3) (a) Patrickios, C. S.; Hertler, W. R.; Abbott, N. L.; Hatton, T. A. *Macromolecules* **1994**, *27*, 930. (b) Creutz, S.; Teyssié, Ph.; Jérôme, R. *Macromolecules* **1997**, *30*, 6. (c) Bütün, V.; Billingham, N. C.; Armes, S. P. *J. Am. Chem. Soc.* **1998**, *120*, 12135. (d) Vamvakaki, M.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1999**, *32*, 2088.

(4) (a) Ohno, K.; Tsuji, Y.; Fukuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2473. (b) Ejaz, M.; Ohno, K.; Tsuji, Y.; Fukuda, T. *Macromolecules* **2000**, *33*, 2870.

(5) (a) Nwankwo, I.; Xia, D. W.; Smid, J. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 581. (b) Vyavahare, N. R.; Kulkarni, M. G.; Mashelkar, R. A. *J. Membr. Sci.* **1990**, *54*, 205. (c) Vázquez, B.; Gurruchaga, M.; Goni, I.; Narvarte, E. *Polymer* **1995**, *36*, 3327. (d) Teraya, T.; Takahara, A.; Kajiyama, T. *Polymer* **1990**, *31*, 1149. (e) Takahara, A.; Teraya, T.; Kajiyama, T. *Polym. Bull. (Berlin)* **1990**, *24*, 333.

(6) (a) Wang, X.-S.; Lascelles, S. F.; Jackson, R. A.; Armes, S. P. *Chem. Commun.* **1999**, 1817. (b) Wang, X.-S.; Armes, S. P. *Macromolecules* **2000**, *33*, 6640. (c) Perruchot, C.; Khan, M. A.; Kamitsi, A.; Armes, S. P.; von Werne, T.; Patten, T. E. *Langmuir* **2001**, *17*, 4479.

(7) (a) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163. (b) Fujishige, S.; Kubota, K.; Ando, I. *J. Phys. Chem.* **1989**, *93*, 3311. (c) Ganachaud, F.; Monteiro, M. J.; Gilbert, R. G.; Dourges, M.-A.; Thang, S. H.; Rizzardo, E. *Macromolecules* **2000**, *33*, 6738. (d) Ishizone, T.; Ito, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4328.

(8) (a) Eggart, M.; Freitag, R. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 803. (b) Kobayashi, M.; Okuyama, S.; Ishizone, T.; Nakahama, S. *Macromolecules* **1999**, *32*, 6466.

(9) (a) Aoshima, S.; Oda, H.; Kobayashi, E. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2407. (b) Forder, C.; Patrickios, C. S.; Armes, S. P.; Billingham, N. C. *Macromolecules* **1996**, *29*, 8160. (c) Aoshima, S.; Sugihara, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3962. (d) Aoshima, S.; Hashimoto, K. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 746.

(10) Ishizone, T.; Han, S.; Okuyama, S.; Nakahama, S. *Macromolecules* **2003**, *36*, 42.

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

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

(13) It is recently reported that atom transfer radical polymerization of MOEGMA gives the polymer with relatively narrow molecular weight distribution ($M_w/M_n = 1.2-1.3$). However, the pendant oligo(ethylene glycol) unit of the employed MOEGMA has a distribution, and the relationship between molecular structure and property of poly(MOEGMA) has not been clarified yet. See ref 6.

(14) (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.

(15) (a) Ozaki, H.; Hirao, A.; Nakahama, S. *Macromol. Chem. Phys.* **1995**, *196*, 2099. (b) Ishizone, T.; Yoshimura, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1998**, *31*, 8706.

(16) 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.

(17) The observed M_n values increased with increasing the monomer-to-initiator ratios, while the apparent deviation in M_n value was observed (Table 1. run 10). 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.

(18) (a) Ozaki, H.; Hirao, A.; Nakahama, S. *Macromolecules* **1992**, *25*, 1391. (b) Hild, G.; Lamps, J. P.; Rempp, P. *Polymer* **1993**, *34*, 2875. (c) Zhang, H.; Ruckenstein, E. *Macromolecules* **1998**, *31*, 746. (d) Zhang, H.; Ruckenstein, E. *Macromolecules* **2001**, *34*, 3587. (e) Sugiyama, K.; Azuma, H.; Watanabe, T.; Ishizone, T.; Hirao, A. *Polymer*, in press.

(19) (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.

(20) (a) Ishizone, T.; Uehara, G.; Hirao, A.; Nakahama, S.; Tsuda, K. *Macromol. Chem. Phys.* **1998**, *199*, 1827. (b) Ishizone, T.; Sugiyama, K.; Sakano, Y.; Mori, H.; Hirao, A.; Nakahama, S. *Polym. J.* **1999**, *31*, 983. (c) Ishizone, T.; Tajima, H.; Torimae, H.; Nakahama, S. *Macromol. Chem. Phys.* **2002**, *203*, 2375. (d) Ishizone, T.; Takata, T.; Kobayashi, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1335.

(21) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiely: New York, 1989; p VI 218.

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

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

(24) For example, see: Hatada, K.; Ute, K.; Tanaka, K.; Okamoto, Y.; Kitayama, T. *Polym. J.* **1986**, *18*, 1037.

MA0347971