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Notes

Anionic Polymerizations of Oligo(ethylene glycol) Alkyl Ether Methacrylates: Effect of Side Chain Length and ω-Alkyl Group of Side Chain on Cloud Point in Water

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Introduction

Water-soluble polymers have attracted a great deal of attention, since they have practical potentials to the industrial applications such as dispersants, stabilizers, emulsifiers, and flocculants. Various water-soluble polymethacrylates have been so far synthesized by introducing the polar and hydrophilic functionalities on the ester moieties to provide the water solubility. In particular, well-defined water-soluble polymethacrylates bearing 2,3-dihydroxypropyl[1] and 2-(*N,N*-dialkylamino)ethyl groups[2] and glucose[3] and oligo(ethylene glycol) functionalities[4] are prepared via the various living polymerizations and the following chemical modifications.

Recently, we have succeeded in the living anionic polymerizations of oligo(ethylene glycol) methyl ether methacrylates, **M1**−**M3** (Chart 1).[5–9] The polymerizations proceeded quantitatively to give the polymers possessing the predicted molecular weights and narrow molecular weight distributions (MWD, $M_w/M_n < 1.1$). Although poly(**M1**), an ethylene glycol ester, was not soluble in water, poly(**M2**) and poly(**M3**) bearing longer oligo(ethylene glycol) side chains showed the solubility in water. Moreover, the aqueous solutions of poly(**M2**) and poly(**M3**) presented the reversible phase transition behaviors at 26 and 52 °C, respectively. These clearly indicate the effect of side-chain length not only on the water solubility but also on the cloud points in water. A similar effect of side chain length on the cloud points has been recently reported on the poly(vinyl ether)s,[10] polyacrylates,[11] and polystyrene derivatives.[11,12] It should be also noted that the poly[di(ethylene glycol) methacrylate] and poly[tri(ethylene glycol) methacrylate] with OH terminal groups in the side chains were readily soluble in water at 0–95 °C and showed no lower critical solution temperature (LCST).[4,13] This shows the significant effect of ω-functionality in the side chain toward the water solubility of polymers. Apparently, the polar hydrophilic OH terminals afford the water solubility of poly[oligo(ethylene glycol) methacrylate]s higher than the methyl ether counterparts, poly(**M2**) and poly(**M3**). In other words, the hydrophobic methyl group decreased the water solubility and induced the phase separation at higher temperature. Thus, the balance between hydrophilicity and hydrophobicity in the structure is essential to attain the thermosensitivity of water-soluble polymethacrylates as previously demonstrated using NMR and IR measurements.[5,14]

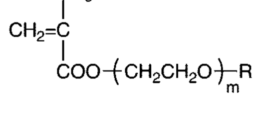
In this Note, we have purposefully synthesized and polymerized a series of alkyl ethers of oligo(ethylene glycol) methacrylates (Chart 1) to clarify the effect of side chain length and ω-functionality on the water solubility and the cloud points, in comparison with our previous report.[5] We newly synthesized a methacrylic acid ester of tetra(ethylene glycol) methyl ether, **M4**, in order to further increase the hydrophilicity by the longer oligo(ethylene glycol) chain. More importantly, a series of ethyl ethers of oligo(ethylene glycol) methacrylates, **E1**−**E4**, were polymerized anionically to demonstrate the effect of hydrophobic ω-alkyl group of side chain compared with the corresponding methyl ethers, **M1**−**M4**.

Results and Discussion

Anionic Polymerization of Monomers. We synthesized novel monomers **M4**, **E3**, and **E4** by the reactions of methacryloyl chloride and the corresponding oligo(ethylene glycol) monoalkyl ethers, while **E1** and **E2** were commercially available. In order to synthesize **E4**, tetra(ethylene glycol) monoethyl ether was prepared by the Williamson reaction of tetra(ethylene glycol) with ethyl iodide in 30% yield. All the resulting methacrylic acid esters were liquid monomers and were purified by the column chromatography and the repeating fractional vacuum distillations over CaH_2.

The anionic polymerizations of methacrylate monomers, **M4** and **E1**−**E4**, were carried out in THF at −78 °C (Table 1, runs 4–12), as previously reported in the cases of **M1**−**M3** (runs 1–3).[5] The binary initiator system of diphenylmethylpotassium

Chart 1



$CH_2{=}C(CH_3)\text{-}COO\text{-}(CH_2CH_2O)_m\text{-}R$

M1: R = Me, m = 1
M2: R = Me, m = 2
M3: R = Me, m = 3
M4: R = Me, m = 4

E1: R =Et, m = 1
E2: R = Et, m = 2
E3: R = Et, m = 3
E4: R = Et, m = 4

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

					$10^{-3}M_n$			tacticity (%)[e]		
run	monomer type, mmol	initiator type, mmol	additive type, mmol	time(h)	calcd[b]	obsd[c]	M_w/M_n[d]	*mm*	*mr*	*rr*
1[f]	**M1**, 9.19	Ph_2CHK, 0.104	Et_2Zn, 1.75	2	13	14	1.04	13	52	35
2[f]	**M2**, 5.93	Ph_2CHK, 0.0702	Et_2Zn, 1.48	2	16	17	1.09	18	48	34
3[f]	**M3**, 3.38	Ph_2CHK, 0.0547	Et_2Zn, 1.33	4	15	16	1.05	4	36	60
4	**M4**, 2.32	Ph_2CHK, 0.0968	Et_2Zn, 1.54	4	6.8	8.4	1.06	6	29	65
5	**M4**, 3.82	Ph_2CHK, 0.0599	Et_2Zn, 1.03	16	18	18	1.09	5	35	60
6	**E1**, 6.34	Ph_2CHK, 0.0967	Et_2Zn, 1.09	3	11	12	1.03	7	56	37
7	**E1**, 5.77	**1**, 0.0810	LiCl, 0.370	3	11	13	1.03	3	24	73
8	**E2**, 4.91	Ph_2CHK, 0.0734	Et_2Zn, 1.65	3	14	17	1.04	20	49	31
9	**E2**, 9.19	**1**, 0.0872	LiCl, 0.403	3	12	15	1.04	6	26	68
10	**E3**, 4.11	Ph_2CHK, 0.0955	Et_2Zn, 1.65	6	11	11	1.04	3	38	59
11	**E3**, 4.32	**1**, 0.0910	LiCl, 0.486	3	12	14	1.04	5	25	70
12	**E4**, 1.97	Ph_2CHK, 0.0583	Et_2Zn, 1.00	16	10	8.9	1.07	6	33	64
13	**M2**, 4.96;**M3**, 3.88	Ph_2CHK, 0.130	Et_2Zn, 1.53	12	14	13	1.04	12	35	53
14	**E2**, 5.28; **E3**, 4.54	Ph_2CHK, 0.159	Et_2Zn, 2.05	12	14	12	1.01	8	39	53

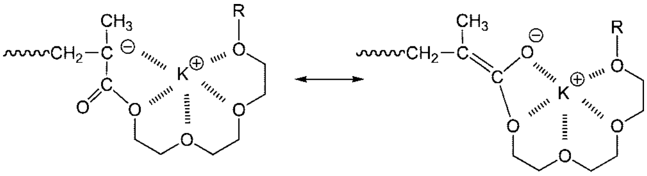
[a] Yield ~100%. [b] M_n(calcd) = (MW of monomer) × [monomer]/[initiator] + (MW of initiator residue). [c] M_n(obsd) was determined by the end-group analysis using ^{1}H NMR. [d] M_w/M_n was determined by the SEC calibration using standard PMMA samples. [e] The triad tacticity was estimated from the ^{13}C NMR signal intensity of quaternary carbons of polymers. [f] Data from ref 5.

(Ph_2CHK) and 11–22-fold of diethylzinc (Et_2Zn)[15] was employed. All the polymerizations quantitatively proceeded to give the polymers possessing predictable molecular weights based on the molar ratios between monomers to initiators within 16 h, even in the cases of **M4** and **E4**, macromonomers possessing longer and bulky tetra(ethylene glycol) side chains. The size exclusion chromatography (SEC) curves of polymers were unimodal and sharp, and the polydispersity indexes, M_w/M_n, were always within 1.1, indicating the narrow MWD. The polymerizations of **E1**−**E3** were also performed with 1,1-diphenyl-3-methylpentyllithium (**1**), an adduct of *s*-BuLi and 1,1-diphenylethylene, in the presence of 5-fold LiCl[16] in THF at −78 °C for 3 h. The organolithium initiator similarly gave the polymers with well-defined chain structures. Thus, the controlled polymerizations of **M4** and **E1**−**E4** were successfully achieved to afford the tailored polymers, similar to the cases of **M1**−**M3**.[5]

The stereoregularity of the polymers was determined by the relative signal intensity of main chain quaternary carbons appearing at 44.9–46.3 ppm in the ^{13}C NMR spectra.[17] The triad tacticities are shown in Table 1. The poly(**E1**−**E3**)s obtained with organolithium initiator in THF possessed syndiotactic configurations regardless of the length of oligo(ethylene glycol) units. This is consistent with the previous reports observed in the polymerizations of various methacrylates including **M1**−**M3** under the similar polymerization conditions.[4,5,16,18] On the other hand, the poly(**E1**) and poly(**E2**) obtained with Ph_2CHK/Et_2Zn had *mr*-rich configurations, indicating almost atactic stereoregularity.

Interestingly, the *mr* contents decreased and the *rr* contents alternatively increased with increasing the lengths of oligo(ethylene glycol) units. The poly(**E3**) and poly(**E4**) bearing longer oligo(ethylene glycol) moieties possessed *rr*-rich configurations. We have already observed a similar tendency in the polymerizations of **M1**−**M3** (see runs 1–3).[5] The plausible explanation for this polymerization behavior is that an association of the multidentate oligo(ethylene glycol) alkyl ether moieties occurs with potassium ion at the propagating chain ends (Scheme 1), as is considered in the cases of glymes. The longer units of **M3**, **M4**, **E3**, and **E4** would form stronger and bulkier propagating species at the terminal to change the tacticity of polymers compared with the methacrylates bearing shorter ethylene glycol and di(ethylene glycol) units. As a consequence, the stereoregularities of polymers possessing tri(ethylene glycol) and tetra(ethylene glycol) side chains are always predominantly *rr*-rich regardless of the counterion of initiators. Thus, the side chain length certainly affects the stereoregularities of the poly[oligo(ethylene glycol) methacrylate]s.

Scheme 1



Random Copolymerization. We next attempted to synthesize random copolymers via the one-pot copolymerization of **M2** and **M3** or **E2** and **E3** (Table 1, runs 13 and 14).[19] In these polymerizations, the reactivity ratio and polymerization rate of oligo(ethylene glycol) methacrylates are assumed to be equal regardless of the difference in the side chain lengths of comonomers.[20] A mixture of **M2** (56 mol %) and **M3** (44 mol %) was polymerized with Ph_2CHK/Et_2Zn in THF at −78 °C. An average side chain length of copolymer was calculated to be 2.4. The copolymerization was completed within 12 h, and a copolymer with a controlled M_n and narrow MWD was obtained quantitatively. A similar well-defined copolymer yielded in the one-pot copolymerization of **E2** (54 mol %) and **E3** (46 mol %). The average side chain length of poly(**E2**-*ran*-**E3**) was 2.5. Since the commercially available oligo(ethylene glycol) alkyl ether methacrylates possess the distribution in the side chain length, these random copolymers are typical model polymers in order to estimate the cloud points of polymers having distribution of side chain lengths.

Solubility and Cloud Point of Polymers in Water. The polymer samples synthesized in this study are advantageous to investigate the solution properties of polymers, since they possess narrow MWDs and controlled M_n values between 8900 and 18 000. The solubilities of polymers are shown in Table 2 in addition to those of poly(**M1**)−poly(**M3**) synthesized previously.[5] All polymers showed good solubility in the various solvents, but they were insoluble in hexane. Methyl ethers, poly(**M1**)−poly(**M4**), were insoluble in diethyl ether, whereas the corresponding ethyl ethers, poly(**E1**)−-poly(**E4**), were soluble in ether, indicating the small but confident effect of terminal functionality of the side chain in the repeating units. In addition, poly(**E1**) was soluble in methanol and ethanol, but the methyl ether counterpart, poly(**M1**), was insoluble in the both polar solvents. The flexible ethyl substituent might induce

Table 2. Solubility of Polymers (I = Insoluble; S = Soluble)

solvent	poly(**M1**)	poly(**M2**)	poly(**M3**)	poly(**M4**)	poly(**E1**)	poly(**E2**)	poly(**E3**)	poly(**E4**)
hexane	I	I	I	I	I	I	I	I
benzene	S	S	S	S	S	S	S	S
$CHCl_3$	S	S	S	S	S	S	S	S
acetone	S	S	S	S	S	S	S	S
ethyl acetate	S	S	S	S	S	S	S	S
Et_2O	I	I	I	I	S	S	S	S
1,4-dioxane	S	S	S	S	S	S	S	S
THF	S	S	S	S	S	S	S	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	S
MeOH	I	S	S	S	S	S	S	S
water	I	S[a]	S[b]	S[c]	I	S[d]	S[e]	S[f]

[a] $T_c \sim 26$ °C. [b] $T_c \sim 52$ °C. [c] $T_c \sim 68$ °C. [d] $T_c \sim 4$ °C. [e] $T_c \sim 27$ °C. [f] $T_c \sim 42$ °C.

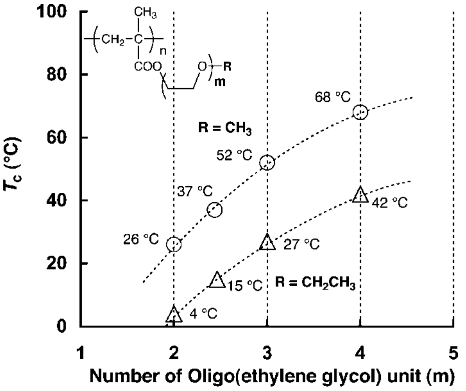


Figure 1. Relationship between number of oligo(ethylene glycol) unit (*m*) and cloud point. Data of methyl and ethyl ethers were plotted with ○ and △, respectively. The cloud points of 0.2 wt % of polymer solutions in water were measured at a heating rate of 0.3 °C min^{-1}.

a higher solubility compared with the methyl counterpart. In terms of the chain length, poly(**M1**) and poly(**E1**), the esters of ethylene glycol, were insoluble in water, similar to the case of poly(2-hydroxyethyl methacrylate) having an OH terminal group on the side chain.[18] By contrast, the polymers possessing longer oligo(ethylene glycol) units, poly(**M2**)−poly(**M4**) and poly(**E2**)−poly(**E4**), were certainly soluble in water.

Interestingly, the aqueous solutions of these polymers presented the typical LCSTs on either heating or cooling process. The phase transition behaviors were quite sensitive ($\Delta T \sim$ 2–6 °C) and reversible (Supporting Information). The hysteresis of the transition in the heating and cooling scan was usually small and was within 3 °C as previously reported.[5] Figure 1 shows the relationship between the side chain length of polymers and the cloud points (T_c). The side chain length of oligo(ethylene glycol) unit clearly affects the T_c of the resulting polymers as well as the stereoregularity as described above. The T_c of poly(**M4**) was observed at 68 °C. This is significantly higher than those of poly(**M2**) and poly(**M3**), T_c = 26 and 52 °C,[5,6e] showing the effect of side chain length. On the other hand, the poly(**E2**) was only soluble in cold water below 4 °C. The observed T_c values of poly(**E2**), poly(**E3**), and poly(**E4**) were 4, 27, and 42 °C and continuously increased with the side chain length. The T_c values of ethyl ethers were ca. 22–26 °C lower than those of the corresponding methyl ethers, supporting that the terminal ethyl group was more hydrophobic compared with the methyl group. A similar tendency on the *ω*-functionality has been reported in the T_c observation of several poly(vinyl ether)s with oligo(ethylene glycol) side chain.[10] The hydrophobic ethyl terminals might prohibit the effective hydration toward the side chain and induce the LCSTs lower than the methyl counterparts. One can predict the T_c values of polymers from the number of oligo(ethylene glycol) units, *m*, by the extrapolation of Figure 1. In the preceding section, we have synthesized two random copolymers of **M2** and **M3** (m = 2.4) and **E2** and **E3** (m = 2.5) by regulating the weight composition of comonomers to be equal. In fact, the T_c values of poly(**M2**-*ran*-**M3**)[19] and poly(**E2**-*ran*-**E3**) were observed at 37 and 15 °C, respectively. These values were intermediate between the corresponding homopolymers and were in good accordance with the T_cs predicted from Figure 1.

In conclusion, we have succeeded in the synthesis of a series of poly[oligo(ethylene glycol) alkyl ether methacrylate]s with well-defined chain structures via the anionic polymerizations. The polymers bearing di-, tri-, and tetra(ethylene glycol) units are soluble in water and show the typical LCSTs in the aqueous solutions. The T_c value of polymers increases with the side chain length of oligo(ethylene glycol) unit[5,10–12] and reaches 68 °C in the case of tetra(ethylene glycol) methyl ether. The methyl terminal substituent induces the higher T_c values compared to those of the hydrophobic ethyl ether counterparts.[10] Now, one can easily predict and tune the T_c values of polymers over the range from 4 to 68 °C by changing the length and terminal functionality in the oligo(ethylene glycol) side chain. We believe that our present result provides new important information on the molecular design of the water-soluble thermosensitive polymethacrylates.

Experimental Section

Materials. All reagents were purchased from Tokyo Kasei, unless otherwise stated, and purified in the usual manner. Monomers **E1** (Aldrich) and **E2** (Nippon Oil Fat) were purified by column chromatography (silica gel, hexane/ethyl acetate) and by the following fractional distillations from CaH_2 in vacuo. Commercially available methacryloyl chloride was used without purification. Tri(ethylene glycol) ethyl ether and tetra(ethylene glycol) methyl ether were dried and distilled over CaH_2 under the reduced pressure. Tetra(ethylene glycol) ethyl ether was synthesized by the reaction of tetra(ethylene glycol) and ethyl iodide in the presence of KOH in THF. Triethylamine 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. Et_2Zn (Tosoh-Akzo) was distilled under the reduced pressure and diluted with dry THF. Trioctylaluminum (Sumitomo Chemical Industry) was diluted with dry heptane. 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. Commercially available *s*-BuLi (1.3 M in cyclohexane, Nacalai Tesque Inc.) was used without purification and diluted with dry heptane. Ph_2CHK were prepared by the reaction of potassium naphthalenide with a 1.1-fold excess of diphenylmethane in THF at room temperature for 48 h. 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]

2-[2-(2-(2-Ethoxyethoxy)ethoxy)ethoxy]ethyl Methacrylate (E4). A solution of methacryloyl chloride (6.75 g, 64.6 mmol) in ether (20 mL) was added dropwise to a mixture of tetra(ethylene glycol) ethyl ether (12.7 g, 57.2 mmol), triethylamine (10.0 g, 99.0 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 a precipitated triethylamine hydrochloride. The filtrate was concentrated under the reduced pressure, and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 10/3–10/6). Vacuum distillation in the presence of CaH_2 and trace amount of methylene blue gave a colorless liquid of **E4** (2.20 g, 7.59 mmol, 13%, bp 125–130 °C/0.3 mmHg). ^1H NMR ($CDCl_3$): δ 1.17 (t, $J = 7.0$ Hz, 3H, $\mathrm{CH_2C}\mathit{H_3}$), 1.91 (s, 3H, $-CH_3$), 3.51 (q, $J = 7.0$ Hz, 2H, $\mathrm{C}\mathit{H_2}\mathrm{CH_3}$), 3.62 (m, 12H, $\mathrm{OC}\mathit{H_2}\mathrm{C}\mathit{H_2}\mathrm{OC}\mathit{H_2}\mathrm{C}\mathit{H_2}\mathrm{OC}\mathit{H_2}\mathrm{C}\mathit{H_2}\mathrm{OCH_2CH_3}$), 3.71 (t, $J = 4.8$ Hz, 2H, $\mathrm{COOCH_2C}\mathit{H_2}$), 4.26 (t, $J = 4.8$ Hz, 2H, $\mathrm{COOC}\mathit{H_2}$), 5.54 and 6.09 (2s, 2H, $\mathrm{C}\mathit{H_2}=$). ^{13}C NMR ($CDCl_3$): δ 15.2 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 18.4 ($\alpha$-$CH_3$), 63.9 ($\mathrm{COO}\mathit{C}\mathrm{H_2}$), 66.7 ($\mathit{C}\mathrm{H_2CH_3}$), 69.2 ($\mathrm{COOCH_2}\mathit{C}\mathrm{H_2}$), 69.9 and 70.7 ($\mathrm{COOCH_2CH_2O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2OCH_2CH_3}$), 125.8 ($CH_2=$), 136.2 ($CH_2=C$), 167.5 ($C=O$). Anal. Calcd for $C_{14}H_{26}O_6{:}0.22H_2O$ (hygroscopic): C, 57.16, H, 8.85. Found: C, 57.16, H, 8.43.

Other novel monomers, **M4** and **E3**, were similarly synthesized in 27 and 38% yields by the reactions of methacryloyl chloride and the corresponding oligo(ethylene glycol) alkyl ethers in diethyl ether in the presence of triethylamine. For the spectroscopic data, see Supporting Information.

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.[21] A typical polymerization procedure (Table 1, run 11) was as follows: A THF solution (4 mL) of 1,1-diphenylethylene (0.150 mmol) was added to a heptane solution (2 mL) of *s*-BuLi (0.0910 mmol) through the break-seal at −78 °C. After 20 min, LiCl (0.486 mmol) in THF (7 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 **E3** (4.32 mmol) in THF (12 mL) was rapidly added to the initiator system at −78 °C through the break-seal with vigorous shaking of the apparatus. After standing at −78 °C for 3 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 a poly(**E3**) (100%, $M_n = 14\,000$, $M_w/M_n = 1.04$).

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 ^1H and ^{13}C NMR spectroscopies (Supporting Information).

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 ^{13}C NMR integral ratio of quaternary carbons appearing at 45.1–46.1 ppm. Three signals were assigned as *mm* (46.1 ppm), *mr* (45.5 ppm), and *rr* (45.1 ppm) triads. SEC chromatograms for determination of MWD 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: $2 \times 10^3 - 4 \times 10^6$) and with ultraviolet (254 nm) or refractive index detection. Cloud points of polymers 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) either at a heating or a cooling rate of 0.3 °C min^{-1}.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) It has been also reported that atom transfer radical polymerization of oligo(ethylene glycol) methyl ether methacrylates gives the polymers with relatively narrow MWDs ($M_w/M_n = 1.2–1.3$). (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) Lutz, J.-F.; Hoth, A. *Macromolecules* **2006**, *39*, 893. (d) Lutz, J.-F.; Akdemir, O.; Hoth, A. *J. Am. Chem. Soc.* **2006**, *128*, 13046. (e) Yamamoto, S.; Pietrasik, J.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 194.

(7) We have recently found that amphiphilic diblock copolymer of styrene and **M2** or **M3** exclusively exposes the "water-soluble" poly(**M2**) or poly(**M3**) segment to the outermost surface even under the dry conditions. We now consider that the hydrophobic methyl terminals of the hydrophilic oligo(ethylene glycol) side chain of polymer segment predominantly participate in covering the surface to reduce the free energy of the system with the increased configurational entropy by exposing many chain ends to the surface (ref 8). It is noteworthy that those amphiphilic diblock copolymers also show a significant blood compatibility (ref 9).

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(19) Very recently, random copolymers of **M2** and **M3** were synthesized by the atom transfer radical polymerization in ref 6e. The T_c values of poly(**M2**-*ran*-**M3**) increased with the molar fraction of **M3** in the copolymer from 26 to 52 °C. Our observed T_c value of poly((**M2**-*ran*-**M3**) (37 °C) is consistent with that predicted from ref 6e.

(20) Since the reversible sequential copolymerizations between **M2** and **M3** are possible via the crossover reactions to afford the tailored block copolymers, the reactivity of both monomers are considered to be comparable (ref 5).

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