Polymer Journal, Vol. 33, No. 12, pp 939—945 (2001)

Glycoconjugated Polymer II. Synthesis of Polystyrene-*block*-poly-(4-vinylbenzyl glucoside) and Polystyrene-*block*-poly-(4-vinylbenzyl maltohexaoside) *via* 2,2,6,6-Tetramethylpiperidine-1-oxyl-Mediated Living Radical Polymerization

Atsushi NARUMI,† Takeshi MATSUDA, Harumi KAGA,*
Toshifumi SATOH, and Toyoji KAKUCHI††

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060–8628, Japan
**National Institute of Advanced Industrial Science and Technology (AIST), Sapporo 062–8517, Japan*

(Received August 8, 2001; Accepted October 11, 2001)

ABSTRACT: The polymerizations of glycoconjugated monomers, *i.e.*, 4-vinylbenzyl glucoside peracetate **(1a)** and 4-vinylbenzyl maltohexaoside peracetate **(1b)**, were carried out using 2,2,6,6-tetramethylpiperidine-1-oxyl-terminated polystyrene (PS-TEMPO, M_n = 8100 and M_w/M_n = 1.17) as a macromolecular initiator in xylene at 120°C ([**1**]/[PS-TEMPO] = 25). The M_n of the product increased from 9900 to 12700 for the polystyrene-*block*-poly-**1a** (**2a**) and from 14200 to 16200 for the polystyrene-*block*-poly-**1b** (**2b**) with the increasing polymerization time, whereas the M_w/M_n values were constant at 1.13–1.21. The deacetylation of **2a** and **2b** using sodium methoxide in dry-THF provided amphiphilic block copolymers containing glucose and maltohexaose as hydrophilic segments, *i.e.*, polystyrene-*block*-poly(4-vinylbenzyl glucoside) (**3a**) and polystyrene-*block*-poly(4-vinylbenzyl maltohexaoside) (**3b**). The solution property of the block copolymers **3a** and **3b** in toluene (a good solvent for polystyrene) and H_2O (a good solvent for saccharides) varied depending on the weight fraction of the glucose residues (f_g, wt%) in **3**, *i.e.*, **3a** with an f_gs of 4, 10, and 14 wt% formed reversed micelle-like aggregate in toluene, whereas **3a** with an f_g of 17 wt% and **3b** with an f_g of 37 and 50 wt% formed micelle-like aggregates in H_2O.

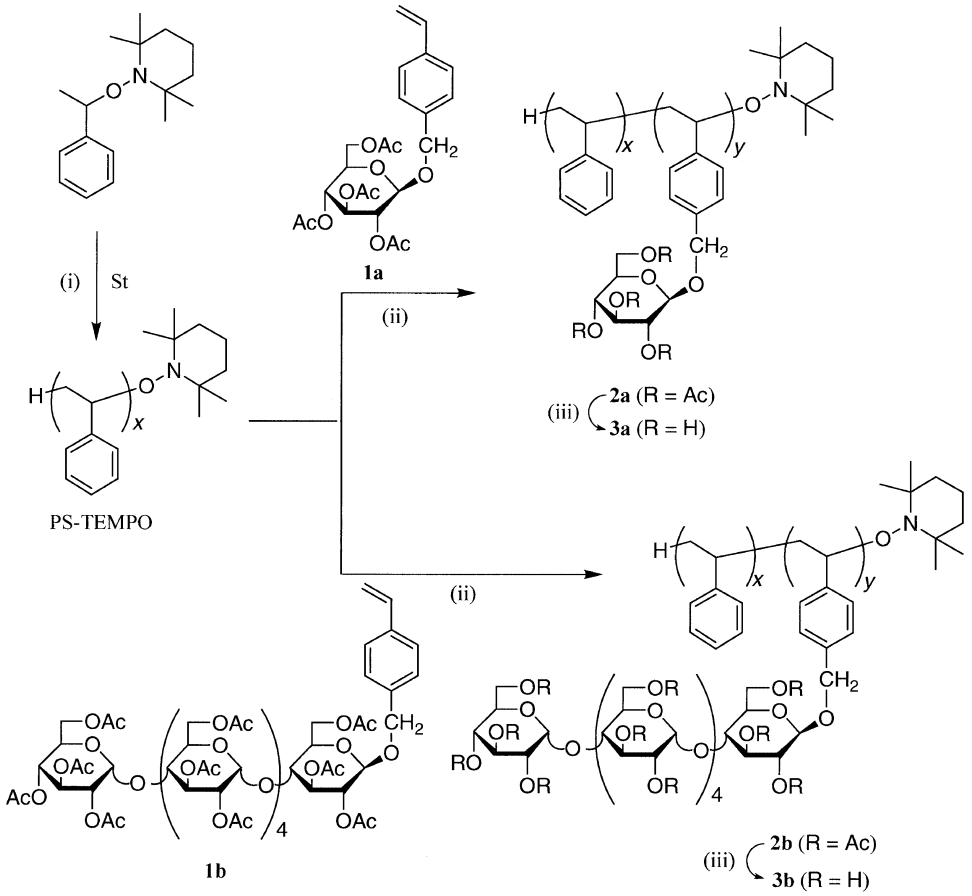
KEY WORDS Block Copolymer / Glucose / Maltohexaose / 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) / Radical Polymerization / Self-Assembling / Polymer Micelle /

The macromolecular design of well-defined glycoconjugated polymers is interesting in terms of the potentiality of biological functions as well as the self-assemble property.[1] Thus precise polymerization systems, such as the ring-opening metathesis[2] and anionic ring-opening polymerizations,[3] have been developed using glycoconjugated monomers. In addition, another common strategy is the living polymerization of a glycoconjugated vinyl monomer, such as the living anionic polymerization of glycoconjugated styrenes[4] and the living cationic polymerization of glycoconjugated vinyl ethers.[5]

Recently, there has been noteworthy progress in living free-radical polymerization,[6] which has advantages for being applicable to a wide variety of functional monomers. Indeed, Fukuda's group reported that glycoconjugated polyacrylates and their block copolymers were synthesized through atom transfer and nitroxide-mediated radical polymerizations.[7] In addition, Li *et al.* reported that block copolymers composed of polystyrene and glycoconjugated polyacrylates are synthesized through the atom transfer radical polymerizations.[8] Although Hawker *et al.* and others reported that the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated living radical polymerization was a way to synthesize well-defined macromolecular architectures, such as block, graft, star-shaped, and hyperbranched polymers,[6c,6e] little is known about the architectures derived from glycoconjugated vinyl monomers prepared through such a useful polymerization system.

In this paper, we present the synthesis of block copolymers consisting of monosaccharides and oligosaccharides as hydrophilic segments, *i.e.*, polystyrene-*block*-poly(4-vinylbenzyl glucoside) **(3a)** and polystyrene-*block*-poly(4-vinylbenzyl maltohexaoside) **(3b)**. The synthetic procedure contains three-steps, (i) the polymerization of styrene using 1-phenyl-1-(2′,2′,6′,6′-tetramethylpiperidine-1′-oxyl)ethane, (ii) the polymerization of 4-vinylbenzyl glucoside peracetate **(1a)** and 4-vinylbenzyl maltohexaoside peracetate **(1b)** using TEMPO-terminated polystyrene (PS-TEMPO) as a macromolecular initiator in xylene, and (iii) the deacetylation of the resulting block copolymers

†JSPS Research Fellowships for Young Scientists.
††To whom correspondence should be addressed (Fax: + 81-11-706-6602, E-mail: kakuchi@poly-mc.eng.hokudai.ac.jp).



Scheme 1. Synthesis of polystyrene-*block*-poly(4-vinylbenzyl glucoside) (**3a**) and polystyrene-*block*-poly(4-vinylbenzyl maltohexaoside) (**3b**): (i) bulk polymerization of styrene (ii) polymerization of 4-vinylbenzyl glucoside peracetate (**1a**) and 4-vinylbenzyl maltohexaoside peracetate (**1b**) using TEMPO-terminated polystyrene (PS-TEMPO) as a macromolecular initiator in xylene, and (iii) deacetylation of block copolymer **2**.

2a and **2b**, as shown in Scheme 1. We also report the solution property of the deacetylated copolymer **3** in appropriate solvents, such as toluene as a good solvent for polystyrene and H_2O for the saccharide.

EXPERIMENTAL

Materials

Styrene (St) (Kanto Chemical Co. Japan, > 99.0%) was distilled prior to use. Xylene and dichloromethane were distilled over CaH_2. 1-Phenyl-1-(2′,2′,6′,6′-tetramethylpiperidine-1'-oxyl)ethane,[9] 4-vinylbenzyl glucoside peracetate (**1a**),[10] and 4-vinylbenzyl maltohexaoside peracetate (**1b**)[10] were prepared according to literature procedures. A seamless cellulose tube (UC24-32-100) was obtained from the Viskase Sales Co.

Measurement

The ^1H and ^{13}C NMR spectra were recorded on a Bruker ASX300 NMR spectrometer. The molecular weights of the resulting polymers were measured using size exclusion chromatography (SEC) at 40°C in tetrahydrofuran (1.0 mL min^{-1}) with a Jasco GPC-900 system equipped with a Waters Ultrastyragel column (linear, 7.8 mm × 300 mm) and two Shodex KF-804L columns (linear, 8 mm × 300 mm). The number-average molecular weight (M_n) was calculated on the basis of a polystyrene calibration. Optical rotations were measured using a Jasco DIP-1000 digital polarimeter. TLC-FID measurements were performed using an Iatron Laboratories IATRON MK-5 with toluene/hexane (4/1) as the mobile phase. The dynamic laser light scattering (DLS) measurement was performed in toluene and H_2O at 22°C using an Otsuka Electronics DLS-7000 light scattering spectrophotometer equipped with an argon ion laser (λ = 488 nm). A scattering angle of 90 degrees was used in this study.

Polystyrene-Capped with TEMPO (PS-TEMPO)

1-Phenyl-1-(2′,2′,6′,6′-tetramethylpiperidine-1′-oxyl)-ethane (250 mg, 0.96 mmol) was dissolved in styrene (25 g, 240 mmol). Air was degassed from the solution by freezing in liquid nitrogen, evacuating the flask, warming to room temperature, and flushing the flask with argon gas. This procedure was repeated three

times. The polymerization mixture was stirred for 5.5 h at 120°C in an oil bath. After cooling, the mixture was diluted with chloroform (25 mL) and then poured into methanol (*ca.* 500 mL). The precipitate was purified by reprecipitation with chloroform-methanol and dried *in vacuo* to give PS-TEMPO as a white powder. Yield, 9.4 g (38%). M_n = 8100, M_w/M_n = 1.17.

*Synthesis of Block Copolymer **2***

A typical procedure is as follows: A solution of PS-TEMPO (0.30 g, 32 μmol) and **1a** (0.37 g, 0.79 mmol) in xylene (2.0 mL) was degassed by the same procedure as that for the preparation of the PS-TEMPO and then stirred for 15 h at 120°C in an oil bath. After cooling, the mixture was diluted with chloroform (*ca.* 2 mL) and then poured into methanol (*ca*. 150 mL). The precipitate was purified by reprecipitation with chloroform-methanol and dried *in vacuo* to give **2a** as a white powder. Yield, 0.36 g (54% based on the total feed). M_n = 9900, M_w/M_n = 1.16, and $[\alpha]_D^{23}$ = −17.4° (*c* 1.0, $CHCl_3$). The composition (*x*-*b*-*y*) was 90-*b*-3, which was estimated from the ^{1}H NMR spectrum.

*Deacetylation of **2***

A typical procedure is as follows: To a solution of **2a** (composition: 90-*b*-3, 0.27 g) in dry THF (5.0 mL) was added 2 wt% sodium methoxide in MeOH/THF (5/95, wt/wt) (2.5 mL). After stirring for 24 h at room temperature, the mixture was poured into water (*ca.* 80 mL), and then transferred to a cellulose tube and dialyzed for 2 days with distilled water. The aqueous suspension was freeze-dried to yield **3a** as a white powder. Yield, 0.24 g (97%). $[\alpha]_D^{23}$ = −11.9° (*c* 0.5, DMSO).

RESULTS AND DISCUSSION

Synthesis of PS-TEMPO

Styrene (St) was polymerized using 1-phenyl-1-(2′,2′,6′,6′-tetramethylpiperidine-1′-oxyl)ethane as an initiator (I) (bulk, [St]/[I] = 250) at 120°C for 5.5 h. In the ^{1}H NMR spectrum of the product (Figure 1, upper line), the signals due to the St units, *i.e.*, the aromatic protons (6.1–7.4 ppm) and the methine and methylene protons (1.4–2.5 ppm) appeared along with the characteristic signal due to the piperidinyloxy methyl protons (1.09, 0.93, 0.41, and 0.21 ppm), indicating that the obtained product was assigned to 2,2,6,6-tetramethylpiperidine-1-oxyl-terminated polystyrene (PS-TEMPO). The number-average molecular weight (M_n), the polydispersity index (M_w/M_n), and the degree of polymerization (x) of PS-TEMPO were 8100, 1.17, and 90, respectively, which were estimated from linear polystyrene-calibrated size exclusion chromatography (SEC) using a differential refractometer (RI) detector (Figure 2, broken line).

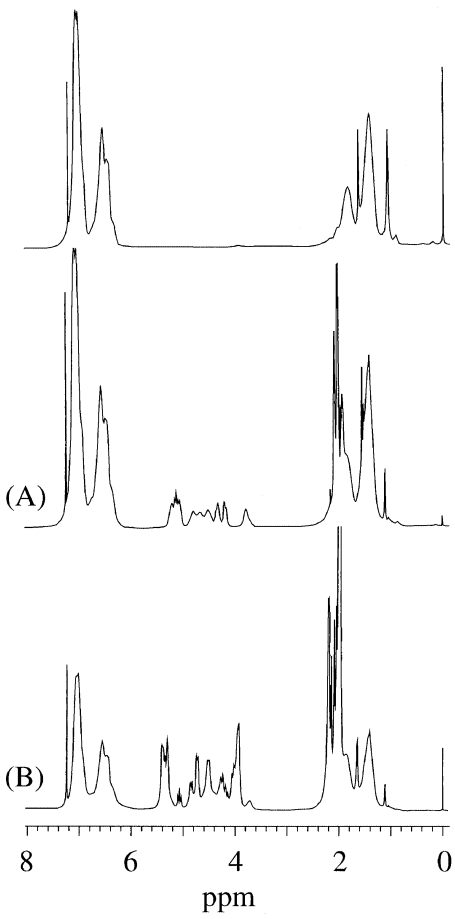


Figure 1. ^{1}H NMR spectra in $CDCl_3$ of (A) **2a** and (B) **2b** obtained from the polymerization of **1a** and **1b** using PS-TEMPO (shown as upper line) as macromolecular initiator for 30 h.

*Synthesis and Characterization of Glycoconjugated Block Copolymer **2***

In general, the bulk polymerization condition was conducted in 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated radical polymerization systems, because the uses of solvent produces a decrease in the polymerization rate and significantly lower the monomer conversion.[9] However, glycoconjugated vinyl monomers, *i.e.*, 4-vinylbenzyl glucoside peracetate **1a** and 4-vinylbenzyl maltohexaoside peracetate **1b**, are both solid monomers, so that an appropriate solvent is needed for the polymerization of PS-TEMPO/**1**. Earlier, xylene was used as a solvent in the kinetic studies of the nitroxide-mediated polymerization system due to its higher boiling temperature, which is suitable for the dissociation between the nitroxide and polymer chain end.[11] Thus, xylene was used for the polymerization of **1** using PS-TEMPO as a macromolecular initiator at 120°C ([**1**]/[PS-TEMPO] = 25). Table I

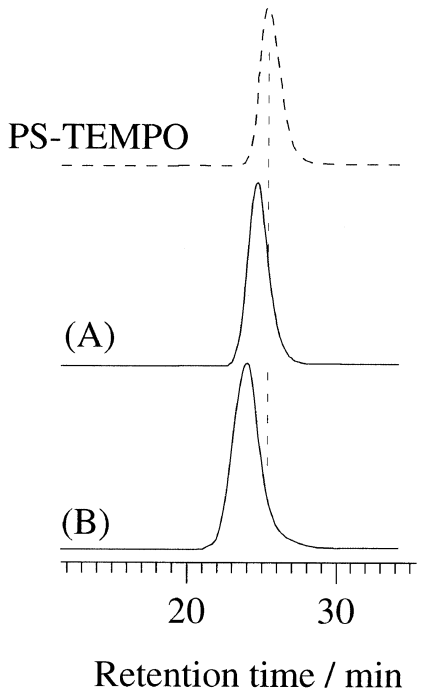


Figure 2. SEC traces of (A) **2a** and (B) **2b** obtained from the polymerization of **1a** and **1b** using PS-TEMPO (shown as upper broken line) as macromolecular initiator for 30 h.

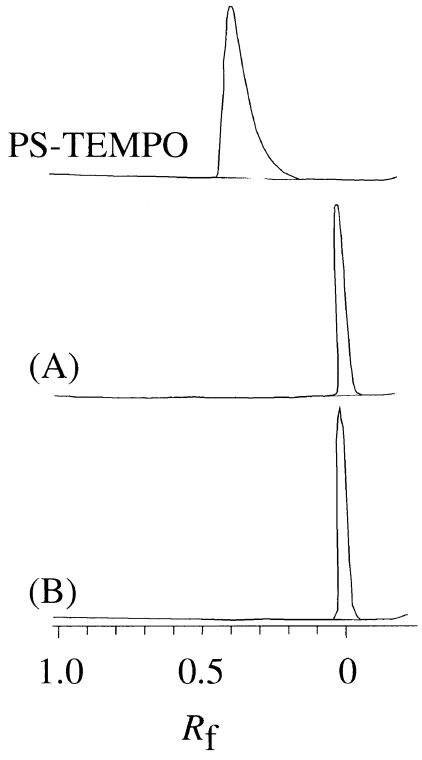


Figure 3. TLC-FID traces of (A) **2a** and (B) **2b** obtained from the polymerization of **1a** and **1b** using PS-TEMPO (shown as upper line) as macromolecular initiator for 30 h.

lists the results of the polymerization of PS-TEMPO/**1** that afforded products **2**. The M_n of the products increased from 9900 to 12700 for **2a** and from 14200 to 16200 for **2b** with the increasing polymerization time, whereas the M_w/M_n values were constant at 1.13–1.21. The values of the specific rotations ($[\alpha]_D^{23}$ *c* 1.0 $CHCl_3$) increased with the increasing polymerization time from −5.7° to −17.4° for **2a** and from +60.1° to +76.0° for **2b**. Unfortunately, a longer reaction time (> 30 h) could not provide neither a significant increase in M_n nor $[\alpha]_D$ values, which might be due to the presence of solvent, resulting in lower monomer conversions.

The SEC chromatogram of **2** displays one peak in Figure 2. However, the elution volumes for **2** were partly overlapped with that of PS-TEMPO, so that the residue of the unreacted PS-TEMPO was confirmed by TLC-FID analysis (SiO_2 plate, toluene/hexane = 4/1, v/v). The peak due to **2** appeared near the spotting points, whereas PS-TEMPO with the R_f value of *ca.* 0.4 was not observed, which were analyzed using a flame ionization detector (TLC-FID) (Figure 3), *i.e.*, PS-TEMPO quantitatively initiated the polymerization of **1**. The SEC and TLC-FID analyses suggested that the TEMPO-mediated radical polymerization was successfully applicable to glycoconjugated vinyl monomers **1** leading to block copolymer **2**, which did not contain any PS-TEMPO along with uncontrolled byproduct such as the homopolymer of **1**.

In the ^{1}H NMR spectra of **2** (Figure 1), the signals due to PS-TEMPO appeared along with the characteristic signals due to the **1** units, *i.e.*, 3.5–6.0 ppm attributed to the methine and methylene protons of the saccharides and 2.0–2.5 ppm to the acetyl protons. The polymerization degree of the **1** unit (y) in **2** was determined by the integration ratio of the signals at 6.1–7.4 ppm and that at 3.5–6.0 ppm in the ^{1}H NMR spectra of **2**. The compositions (x-*b*-y) of **2** are listed in Table I. The polymerization degree of the St unit (x) in **2** is 90, which equals that of PS-TEMPO. The y values of **2a** were very similar to those of **2b**, indicating that there is no essential difference in the polymerization tendency using the PS-TEMPO initiator between **1a** and **1b**. When the molar ratio of **1** and PS-TEMPO ([**1**]/[PS-TEMPO]) was 25 and above, **1** was successfully initiated by PS-TEMPO and polymerized up to the conversion of *ca.* 50%.

*Characteristic Property of Glycoconjugated Block Copolymer **3***

Amphiphilic block copolymers containing glucose and maltohexaose as hydrophilic segments, *i.e.*, polystyrene-*block*-poly(4-vinylbenzyl glucoside) **3a** and polystyrene-*block*-poly(4-vinylbenzyl maltohexaoside) **3b**, were obtained through the deacetylation of **2a** and **2b** using sodium methoxide in dry-THF, respectively. The weight fraction of the glucose residue (f_g, wt%) ranged from 4–17 wt% for **3a** and from 37–

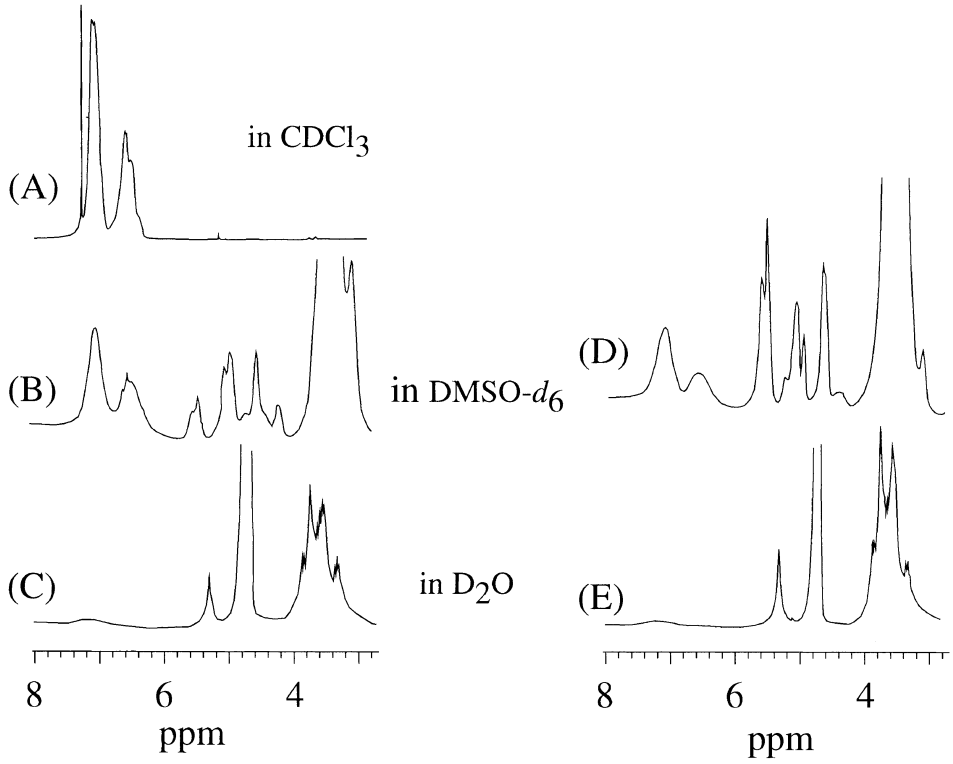


Figure 4. ^{1}H NMR spectra of (A) **3a** with the f_g of 10 in $CDCl_3$, (B) **3a** with the f_g of 17 in DMSO-d_6, (C) **3a** with the f_g of 17 in D_2O, (D) **3b** with the f_g of 37 in DMSO-d_6, and (E) **3b** with the f_g of 37 in D_2O.

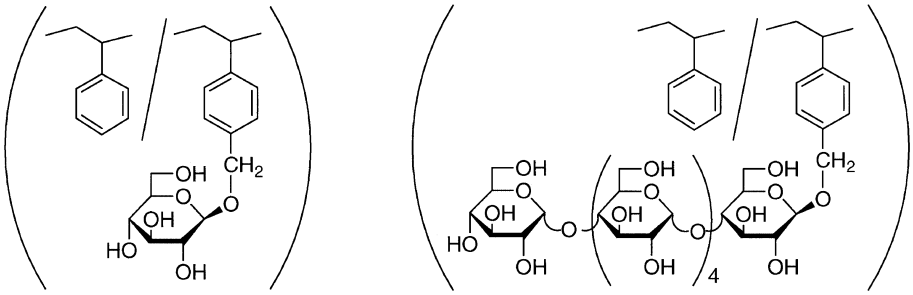
Table I. Polymerization of **1a** and **1b** using PS-TEMPO as a macromolecular initiator leading to poly(St-*b*-**1**) (**2**) and solvent-solubility of glucose- and maltohexaose-conjugated polystyrenes (**3**)

Monomer	Polymer **2**[a]					Polymer **3**[b]		
	Time	M_n[c]	M_w/M_n[c]	$[\alpha]_D$[d]	Composition[e]	Saccharide-contents	Solubility[f]	
	h			deg	*x*-*b*-*y*	f_g, wt%	Toluene	H_2O
1a	10	9900	1.17	− 5.7	90-*b*-3	4	(+)	(−)
	15	10200	1.16	−11.9	90-*b*-6	10	(+)	(±)
	22.5	11700	1.17	−16.4	90-*b*-9	14	(+)	(±)
	30	12700	1.13	−17.4	90-*b*-12	17	(±)	(+)
1b	15	14200	1.18	+60.1	90-*b*-6	37	(±)	(+)
	30	16200	1.21	+76.0	90-*b*-11	50	(±)	(+)

[a]Solvent, xylene; $[\mathbf{1}]_0 = 0.39\,mol\,L^{-1}$; $[\mathbf{1}]_0/[\text{PS-TEMPO}]_0 = 25$. [b]Prepared from polymer **2** through deacetylation using NaOMe in THF. [c]Determined by SEC using polystyrene standards. [d]Measured in $CHCl_3$ at 23°C (*c* 1.0). [e]The *x* value is average-number of the St units; the *y* values are average-number of the **1** units, which were determined by the ^{1}H NMR spectra. [f](−): insoluble, (±): swelled, (+): stably suspended.

50 wt% for **3b** as listed in Table I, which were calculated from the composition of **2a** and **2b**, respectively. The amphiphilic property was observed for the ^{1}H NMR spectra of **3**. The signals due to the saccharide moieties appeared along with that of the aromatic moiety in the ^{1}H NMR spectra of **3a** and **3b** in DMSO-d_6 (Figures 4B and 4D, respectively). On the other hand, the signals due to the saccharide moieties disappeared for **3a** (f_g = 10) in $CDCl_3$ (Figure 4A), whereas the signals due to the aromatic moieties were significantly broadened and disappeared in the ^{1}H NMR spectra of **3a** (f_g = 17) and **3b** in D_2O (Figures 4C and 4E, respectively). These results should be caused by the fact that the intramolecular mobility of the saccharide and polystyrene moieties in **3** were eliminated in their respective poor solvents, *i.e.*, $CDCl_3$ and D_2O.

Table I lists the solubility of **3** in toluene as a good solvent for polystyrene and H_2O as a good solvent for the glucose units. The solubility characteristics of the glucose-conjugated block copolymer **3a** depended on their f_g values and were classified into three major categories, *i.e.*, (−) insoluble, (±) swelled, and (+) suspended giving a stable turbid solution. The hydrophobic/hydrophilic property of **3a** apparently changed at the f_g of *ca.* 15 wt%, *i.e.*, **3a** with the f_g of 4, 10, and 14 wt% in toluene and **3a** with the f_g of 17 wt%



Poly(St-*stat*-4-vinylbenzyl glucoside) (**4a**)

Saccharide-contents	Solubility[a]	
f_g,wt%	Toluene	H_2O
13	(++)	(−)
22	(±)	(−)
32	(−)	(−)
39	(−)	(−)
48	(−)	(±)
52	(−)	(++)

[a](−): insoluble, (±): swelled, (++): soluble.

Poly(St-*stat*-4-vinylbenzyl maltohexaoside) (**4b**)

Saccharide-contents	Solubility[a]	
f_g,wt%	Toluene	H_2O
16	(±)	(−)
28	(−)	(−)
43	(−)	(±)
46	(−)	(++)

[a](−): insoluble, (±): swelled, (++): soluble.

Chart 1. Solubility of poly(styrene-*stat*-4-vinylbenzyl glucoside) (**4a**) and poly(styrene-*stat*-4-vinylbenzyl maltohexaoside) (**4b**).[10]

in H_2O gave turbid solutions classified as (+), which did not produce any precipitate for at least 1 month. Chart 1 summarizes the solubility for poly(styrene-*stat*-4-vinylbenzyl glucoside) (**4a**).[10] It was found that the solubility characteristics of **3a** were significantly different from that for **4a** though their f_g values were very similar. In one example, **3a** with the f_g of 14 wt% gave a stable suspension in toluene (+) and swelled in H_2O (±), while **4a** with the f_g of 13 wt% gave completely clear solutions in toluene (++) and insoluble in H_2O (−). The solubility characteristic for the maltohexaose-conjugated block copolymer **3b** also differed from that for poly(styrene-*stat*-4-vinylbenzyl maltohexaoside) (**4b**)[10] (Chart 1). Although **4b** with the f_g > *ca.* 28 wt% did not swell in toluene (−) and the f_g > *ca.* 46 wt% were soluble in H_2O gave clear aqueous solutions (++), **3b** with the f_g of 37 and 50 wt% produced a stable turbid solution (+) and swelled in toluene (±). These results suggested that the solution property of the block copolymer **3** was extremely different from that of the statistical copolymer **4**, *i.e.*, **3** was stably suspended as ordered intermolecular aggregates, while **4** was soluble without such aggregation or insoluble by forming cross-linked aggregates.

A dynamic laser light scattering (DLS) measurement was carried out in order to characterize the turbid solutions of **3** classified as (+) (Figure 5). All the polymer solutions were clarified using a 0.45 μm millipore filter. The concentrations of **3** were 5 g L^{-1} in toluene, and 0.2 g L^{-1} in water, respectively. The strong scattering intensity was obtained for the turbid toluene solutions of **3a** classified as (+). There were aggregates with diameters of > *ca.* 20 nm for those solutions. The

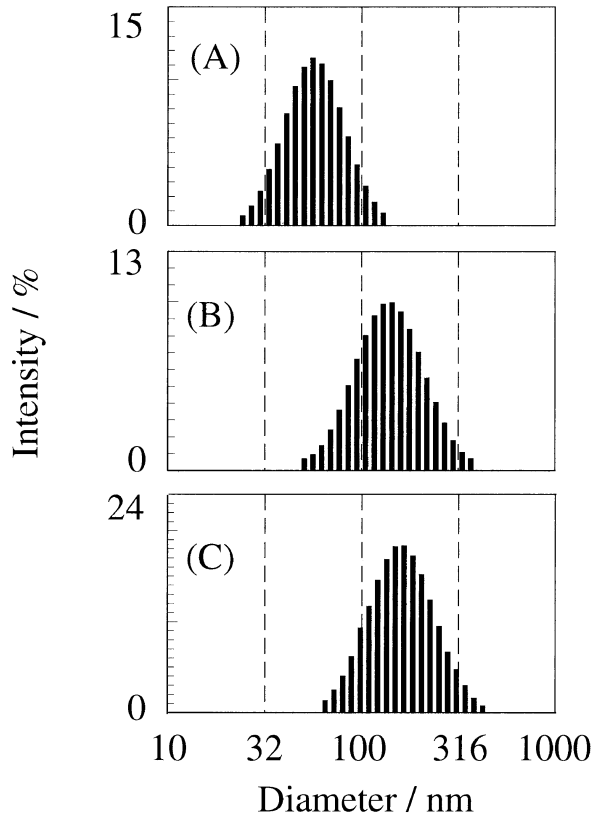


Figure 5. Particle size distribution of (A) **3a** with the f_g of 10 in toluene, (B) **3a** with the f_g of 17 in H_2O, and (C) **3b** with the f_g of 37 in H_2O.

average diameters of the aggregates were 23, 62, and 92 nm for **3a** with the f_g values of 4, 10, and 14, respectively, which were determined by the cumulant analysis. Hence, **3a** should form a stable suspension, which is composed of a hydrophobic polystyrene shell and a hydrophilic saccharide core, *i.e.*, a reversed micelle-

like aggregation. The aggregates with diameters of > *ca*. 50 nm were observed for the aqueous suspensions of **3a** (f_g = 17) and **3b**. The average diameter of the larger aggregates was 123 nm for **3a** (f_g = 17) and *ca*. 135 nm for **3b**. These results indicated that the aqueous suspensions should be composed of a hydrophilic saccharide shell and a hydrophobic polystyrene core, *i.e.*, a micelle-like aggregation.

CONCLUSIONS

The synthesis of block copolymers having glucose and maltohexaose as hydrophilic segments have been studied in relation to their characteristic amphiphilic properties. Saccharide-conjugated styrenes, such as 4-vinylbenzyl glucoside peracetate **1a** and 4-vinylbenzyl maltohexaoside peracetate **1b**, were found to be successfully applicable to the TEMPO-mediated radical polymerization to afford the well-defined glycoconjugated block polymers **2a** and **2b**, respectively. Polystyrene-*block*-poly(4-vinylbenzyl glucoside) (**3a**) and polystyrene-*block*-poly(4-vinylbenzyl maltohexaoside) (**3b**), deacetylated **2a** and **2b**, respectively, exhibited a hydrophobic/hydrophilic property depending on the weight fraction of the glucose residues in **3**, which significantly differed from those for poly(styrene-*stat*-4-vinylbenzyl glucoside) and poly(styrene-*stat*-4-vinylbenzyl maltohexaoside). In addition, **3** formed micelle-like aggregates consisting of a saccharide shell and a polystyrene core in H_2O and reversed micelle-like aggregates consisting of a polystyrene shell and a saccharide core in toluene. Thus the TEMPO-controlled free-radical polymerization was one of the useful tools for constructing well-defined macromolecular architectures, glycoconjugated block copolymers, and their self-assembled structures, such as micelles and reversed micelles, which were controlled by changing the weight fraction of glucose residues in the block copolymers.

Acknowledgment. We would like to thank the Japan Society for the Promotion of Science for their financial support of this research.

REFERENCES

1. Recent review,
M. Okada, *Prog. Polym. Sci.,* **26**, 67 (2001).
2. a) K. H. Mortell, M. Gingras, and L. Kiessling, *J. Am. Chem. Soc*., **116**, 12053 (1994).
b) C. Fraser and R. H. Grubbs, *Macromolecules,* **28**, 7248 (1995).
c) K. Nomura and R. R. Schrock, *Macromolecules,* **29**, 540 (1995).
3. a) K. Aoi, K. Tsutsumiuchi, and M. Okada, *Macromolecules,* **27**, 875 (1994).
b) K. Tsutsumiuchi, K. Aoi, and M. Okada, *Macromolecules,* **30**, 4013 (1997).
4. S. Loykulnant, M. Hayashi, and A. Hirao, *Macromolecules,* **31**, 9121 (1998).
5. a) K. Yamada, M. Minoda, T. Fukuda, and T. Miyamoto, *J. Polym. Sci., Polym. Chem. Ed.,* **39**, 459 (2000).
b) K. Yamada, K. Yamaoka, M. Minoda, and T. Miyamoto, *J. Polym. Sci., Polym. Chem. Ed.,* **35**, 255 (1997).
c) K. Yamada, M. Minoda, and T. Miyamoto, *J. Polym. Sci., Polym. Chem. Ed.,* **35**, 751 (1997).
d) K. Yamada, M. Minoda, and T. Miyamoto, *Macromolecules,* **32**, 3553 (1999).
6. Reviews,
a) M. K. Georges, R. P. N. Vergin, P. M. Kazmaier, and G. K. Hamer, *Trends Polym. Sci.,* **2**, 66 (1994).
b) T. P. Davis, D. Kukulj, D. M. Haddleton, and D. R. Maloney, *Trends Polym. Sci.,* **3**, 356 (1995).
c) C. J. Hawker, *Trends Polym. Sci.,* **4**, 183 (1996).
d) M. Sawamoto and M. Kamigaito, *Trends Polym. Sci.*, **4**, 371 (1996).
e) C. J. Hawker, *Acc. Chem. Res.,* **30**, 373 (1997).
f) K. Matyjaszewski, *Acc. Chem. Res.,* **32**, 895 (1999).
7. a) K. Ohno, Y. Tsuji, T. Miyamoto, T. Fukuda, M. Goto, K. Kobayashi, and T. Akaike, *Macromolecules,* **31**, 1064 (1998).
b) K. Ohno, Y. Tsuji, and T. Fukuda, *J. Polym. Sci., Part A: Polym. Chem.,* **36**, 2473 (1998).
c) K. Ohno, Y. Izu, S. Yamamoto, T. Miyamoto, and T. Fukuda, *Macromol. Chem. Phys.,* **200**, 1619 (1999).
8. Z-C. Li, Y-Z. Liang, and F-M. Li., *Chem. Commun.,* **16**, 1557 (1999).
9. C. J. Hawker, G. G. Barclay, A. Orellana, J. Dao, and W. Devonport, *Macromolecules*, **29**, 5245 (1996).
10. A. Narumi, H. Kaga, K. Kawasaki, Y. Taniguchi, T. Satoh, and T. Kakuchi, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 4061 (2001).
11. K. A. Moffat, G. K. Hamer, and M. K. Georges, *Macromolecules*, **32**, 1004 (1999).