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Synthesis of amphiphilic triblock copolymer of polystyrene and poly(4-vinylbenzyl glucoside) via TEMPO-mediated living radical polymerization

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Abstract

4-Vinylbenzyl glucoside peracetate **1** was polymerized with α,α′-bis(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-1,4-diethylbenzene **2** in chlorobenzene using (1*S*)-(+)-10-camphorsulfonic acid anhydrous (CSA) as an accelerator ([**1**] = 0.4 M,[**1**]/[**2**]/[CSA] = 75/1/1.3) at 125 °C for 5 h. The polymerization afforded poly(4-vinylbenzyl glucoside peracetate) having TEMPO moieties on both sides of the chain ends, **3**, with a molecular weight ($M_{w,SLS}$) of 8500, a polydispersity index (M_w/M_n) of 1.09, and an average degree of polymerization of the **1** unit (x) of 17. Styrene (St) was polymerized with **3** in chlorobenzene at 125 °C (St/chlorobenzene = 1/2, w/w). The polymerization successfully afforded polystyrene–poly(4-vinyl glucoside peracetate)–polystyrene, **4**, when the polymerization time was below about 2 h. Polymer **4** with the $M_{w,SLS}$ of 12,500, 17,900, and 29,400, the compositions ($y-x-y$) of 20–17–20, 45–17–45, and 100–17–100, and the M_w/M_n of 1.12, 1.14 and 1.17 were modified by deacetylation using sodium methoxide in dry-THF into polystyrene–poly(4-vinyl glucoside peracetate)–polystyrene, **5**. The solubility of polymer **5** was examined using a good solvent for polystyrene such as toluene and for the saccharide such as H_2O. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Glycoconjugated polymer; Triblock copolymer; Living radical polymerization

1. Introduction

Much attention has focused on the synthesis of well-defined block copolymers, which are composed of hydrophobic and hydrophilic blocks covalently bonded together, because they possess attractive properties such as the formation of self-assembled aggregates in the appropriate solvent. For example, Eisenberg and co-workers reported that the well-defined AB diblock copolymer of polystyrene and poly(acrylic acid) was synthesized [1] and showed various aggregate morphologies in aqueous solution [2]. Chen and Jenekhe reported that the AB diblock copolymer of polyquinoline and polystyrene was synthesized [3] and found to self-organize into large aggregates with several wonderful abilities [4,5]. Such a self-assemble property is of interest for not only the AB block copolymer but also the ABA triblock copolymer. For example, Brown and co-workers reported that the triblock copolymer composed of poly(ethylene oxide) and polypropylene formed cluster and network structures in solution [6–8]. Chu and co-workers investigated the self-assemble property of triblock copolymers, which were composed of polyoxyethylene, polyoxypropylene, and polyoxybutylene, in aqueous solution using light scattering measurements [9–11]. Chen and Jenekhe reported, in recent years, that the ABA triblock copolymer of polyquinoline and polystyrene was synthesized and formed characteristic self-assemble aggregates [12].

Recently, the synthesis of block copolymers consisting of a vinyl polymer and poly(vinyl saccharide) has seen increased attention, because they have the potential to become new amphiphilic materials due to a block with high water-solubility [13,14]. The AB diblock copolymers of the vinyl polymer and poly(vinyl saccharide) have been successfully prepared using precise synthetic techniques, such as living cationic polymerization [15–18], living anionic polymerization [19], atom transfer radical polymerization [20–22], and nitroxide-mediated living radical

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polymerization [23,24]. There have been few attempts, however, to synthesize the amphiphilic ABA triblock copolymer of a vinyl polymer and poly(vinyl saccharide).

In the article, we report the synthesis of a novel glycoconjugated architecture, i.e. the polystyrene–poly(vinyl saccharide)–polystyrene triblock copolymer. This synthetic procedure is based on the 2,2,6,6-tetramethylpiperidiloxy (TEMPO)-mediated living radical polymerization [25–27]. We polymerized the 4-vinylbenzyl glucoside peracetate (**1**) with α,α′-bis(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-1,4-diethylbenzene (**2**) as an initiator to prepare poly(4-vinylbenzyl glucoside peracetate) having TEMPO on both sides of the chain ends, i.e. the glycoconjugated prepolymer **3**. Styrene was polymerized with **3** in chlorobenzene to synthesize the polystyrene–poly(4-vinyl glucoside peracetate)–polystyrene triblock copolymer, **4**. Polymer **4** was modified by deacetylation into polystyrene–poly(4-vinyl glucoside)–polystyrene, i.e. the glycoconjugated triblock copolymer **5**. The solubility of **5** was examined using appropriate solvents, such as toluene as a good solvent for polystyrene and H_2O for the saccharide.

2. Experimental

2.1. Materials and measurements

Styrene (St) (Kanto Chemical Co., Japan, >99.0%) was distilled prior to use. Chlorobenzene (Kanto Chemical Co., Japan, >99.5%) and THF (Junsei Chemical Co., Japan, >99.0%) were distilled over CaH_2 prior to use. 4-Vinyl glucoside peracetate **1** [28,29] and α,α′-bis(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-1,4-diethylbenzene **2** [30] were prepared according to literature procedures. Anhydrous (1*S*)-(+)-10-camphorsulfonic acid (Kanto Chemical Co., Japan, >98.0%) and 28 wt% sodium methoxide (Wako Pure Chemical Industry, Japan, >99.0%) were used without further purification. The seamless cellulose tube (UC24-32-100) was obtained from the Viskase Sales Co.

The ^1H NMR spectra were recorded on a JEOL JNM-GX270 instrument. The molecular weights of the polymers were measured using size exclusion chromatography (SEC) at 40 °C in chloroform (1.0 ml/min) 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. Specific rotations were measured using a Jasco DIP-1000 digital polarimeter. The static laser light scattering (SLS) measurement was performed in toluene at 25 °C on an Otsuka Electronics DLS-7000 light scattering spectrophotometer ($\lambda = 633$ nm; four-point measurements; $c = 2$–10 mg/ml). The refractive index increment (dn/dc) was measured in toluene at 25 °C on an Otsuka Electronics DRM-1021 double beam-differential refractometer ($\lambda = 633$ nm). The dynamic laser light scattering (DLS) measurement was performed in H_2O at 25 °C using an Otsuka Electronics DLS-7000 light scattering spectrophotometer equipped with an argon ion laser ($\lambda = 488$ nm). A scattering angle of 90° was used in this study. The average diameter of particles was calculated from a cumulant analysis.

2.2. Glycoconjugated prepolymer **3**

4-Vinylbenzyl glucoside peracetate **1** (6.0 g, 13 mmol), α,α′-bis(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-1,4-diethylbenzene **2** (77 mg, 0.17 mmol), and anhydrous (1*S*)-(+)-10-camphorsulfonic acid (CSA) (52 mg, 0.22 mmol) were dissolved in chlorobenzene (32 ml). 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 5.0 h at 125 °C in an oil bath. After cooling, the mixture was diluted with chloroform (ca. 30 ml) and then poured into hexane (ca. 500 ml). The precipitate was purified by reprecipitation with chloroform–hexane and dried in vacuo to give the glycoconjugated prepolymer **3** as a white powder. Yield, 1.4 g (21%). $M_{w,SEC} = 4600$, $M_w/M_n = 1.09$. $M_{w,SLS} = 8500$, $dn/dc = 0.0187$ ml g^{-1}. $[\alpha]_D^{23} = -49.6°$ (c 1.0, $CHCl_3$). The ^1H NMR spectrum of **3** is shown in Fig. 1a. The average degree of polymerization of the **1** unit in **3**, x, was determined from

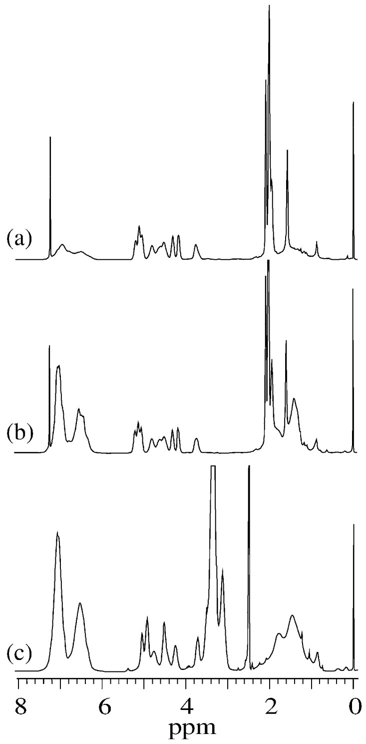
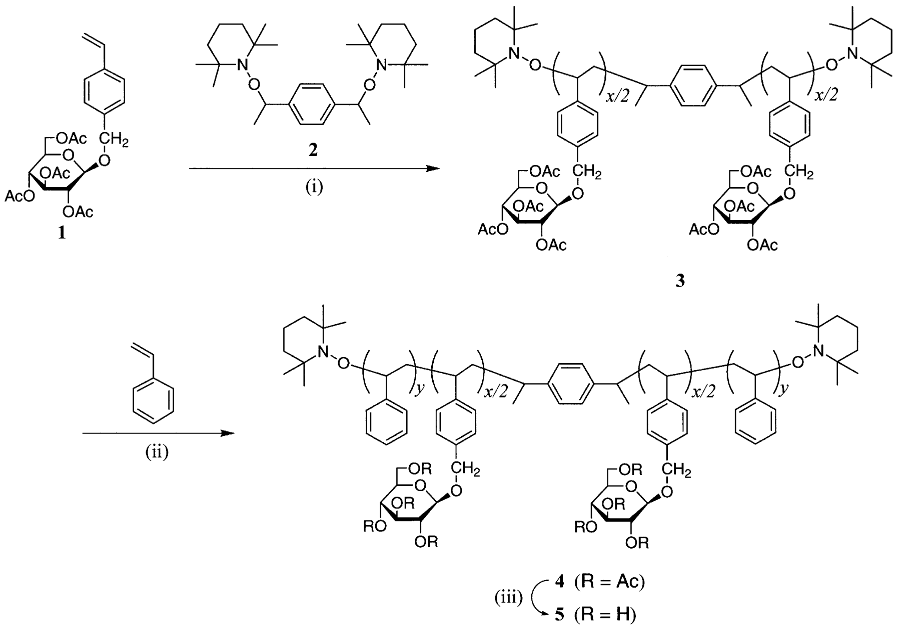


Fig. 1. ^1H NMR spectra of (a) glycoconjugated prepolymer **3**, (b) glycoconjugated triblock copolymer **4-I**, and (c) glycoconjugated triblock copolymer **5-I**.



Conditions: (i) chlorobenzene, CSA, 125 °C; (ii) chlorobenzene, 125 °C; (iii) NaOMe-MeOH, THF

Scheme 1. Synthesis of glycoconjugated triblock copolymer.

the following equation: $x = (M_{\mathrm{w,SLS}}$ of **3** $: 8500 - M_{\mathrm{w}}$ of **2** $: 445)/(M_{\mathrm{w}}$ of **1** $: 464) = 17$.

2.3. Glycoconjugated triblock copolymer 4

A typical procedure is as follows. A solution of **3** (0.21 g, 0.025 mol) and St (1.0 g, 9.9 mmol) in chlorobenzene (2.1 g) was degassed by the same procedure as above and then stirred for 1.0 h at 125 °C. After cooling, the mixture was diluted with chloroform (ca. 4 ml) and then poured into methanol (ca. 200 ml). The precipitate was purified by reprecipitation from chloroform–methanol and dried in vacuo to give the glycoconjugated triblock copolymer **4-I** as a white powder. Yield, 0.31 g (10%). $M_{\mathrm{w,SEC}} = 7800$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.14$. $M_{\mathrm{w,SLS}} = 12{,}500$, $\mathrm{d}n/\mathrm{d}c = 0.0520\ \mathrm{ml\ g^{-1}}$. $[\alpha]_{\mathrm{D}}^{23} = -31.0°$ (c 1.0, $CHCl_3$). The composition (y–x–y) was 20–17–20, which was estimated from the ^{1}H NMR spectrum (Fig. 1b).

2.4. Glycoconjugated triblock copolymer 5

A typical procedure is as follows. To a solution of **4-I** (0.25 g) in dry THF (6 ml) was added three drops of 28 wt% sodium methoxide in MeOH. After stirring for 24 h at room temperature, the mixture was poured into H_2O (ca. 30 ml), and then transferred to a cellulose tube and dialyzed for 2 days with H_2O. The aqueous suspension was freeze-dried to yield the glycoconjugated triblock copolymer **5-I** as a white powder. Yield, 0.18 g (91%). The ^{1}H NMR spectrum of **5-I** is shown in Fig. 1c.

3. Results and discussion

3.1. Synthesis of glycoconjugated prepolymer

The synthetic procedure for glycoconjugated triblock copolymer is based on the 2,2,6,6-tetramethylpiperidiloxy (TEMPO)-mediated living radical polymerizations [25–27] as shown in Scheme 1. In the first step, 4-vinylbenzyl glucoside peracetate **1** was polymerized with α,α′-bis(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-1,4-diethylbenzene **2** in chlorobenzene using anhydrous (1*S*)-(+)-10-camphorsulfonic acid (CSA) as an accelerator ($[\mathbf{1}] = 0.4$ M,$[\mathbf{1}]/[\mathbf{2}]/[\mathrm{CSA}] = 75/1/1.3$) at 125 °C for 5 h. The polymeric product was isolated as a white powder after purification by reprecipitation in chloroform–hexane with the 21% yield. The hexane-soluble species were found to be unreacted **1** as judged by the TLC analysis, which could be easily purified by column chromatography. The yield of the polymeric product was low, because the uses of solvent produces a decrease in the polymerization rate and significantly lower the monomer conversion for TEMPO-mediated radical polymerization systems [31]. In addition, the polymerization time had to be intentionally suppressed to avoid side reactions resulting in a loss of TEMPO functionality.

The polymeric product was characterized by ^{1}H NMR spectroscopy, SEC, and SLS measurement. Fig. 1a shows the ^{1}H NMR spectrum of the product. The signals of the protons due to the aromatic moieties (6.2–7.4 ppm), the saccharide (3.5–5.4 ppm), and the acetyl groups (2.0–2.5 ppm) were observed. Additionally, the characteristic

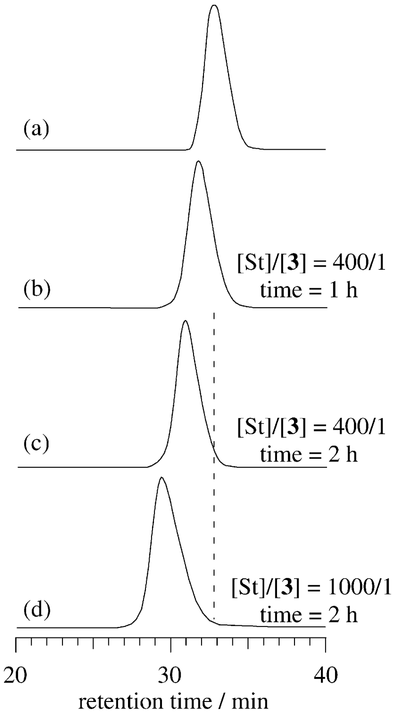


Fig. 2. SEC chromatograms of (a) glycoconjugated prepolymer **3** and (b)–(d) the product obtained from the polymerization of St with **3**.

signal assignable to the piperidinyloxy methyl protons (0.91 ppm) appeared. Fig. 2a shows the SEC chromatogram of the product. The SEC chromatogram displays one peak with the weight-average molecular weight ($M_{w,SEC}$) of 4600, which was estimated from the polystyrene-calibrated SEC using a differential refractometer (RI) detector. The polydispersity index (M_w/M_n) of the product was a low value of 1.09, suggesting that both TEMPO moieties in **2** successfully initiated the polymerization of **1**. The ^{1}H NMR and SEC analyses indicated that the product was assigned to poly(4-vinylbenzyl glucoside peracetate) having TEMPO moieties on both sides of the chain ends, i.e. the glycoconjugated prepolymer **3**.

The $M_{w,SEC}$ value was apparent molecular weight based on polystyrene standards. Thus, the absolute molecular weight of **3** had to be determined for the clarification of the average degree of polymerization of the **1** unit in **3**, x. The weight-average molecular weight determined by the SLS measurements, $M_{w,SLS}$, was 8500 for **3**, corresponding to the x value of 17. This value was completely consistent with the theoretical molecular weight of 8500, which was determined from the isolated yield.

*3.2. Synthesis of glycoconjugated triblock copolymer **4***

The polymerization of styrene (St) was performed with the glycoconjugated prepolymer **3** in chlorobenzene at 125 °C (St/chlorobenzene = 1/2, w/w) as shown in Scheme 1. The product was isolated as a white powder after purification by reprecipitation with chloroform–methanol. The filtrate did not contain any polymeric materials, indicating that the methanol-soluble **3** was quantitatively consumed after the polymerization of St.

The polymerization was attempted using the molar ratio of St and **3** in the feed, [St]/[**3**] of 400/1. Fig. 2b and c show the SEC chromatograms of the products, which shifted to the high molecular weight region with the increasing polymerization time. The chromatograms exhibited one peak with the $M_{w,SEC}$ values of 7800 and 10,700 and the M_w/M_n values of 1.12 and 1.14, when the polymerization times were 1 and 2 h, respectively (Fig. 2b and c). The fact that the M_w/M_n values were small suggested that the St/**3** system proceeded through a controlled manner to afford the polystyrene–poly(4-vinyl glucoside peracetate)–polystyrene, i.e. the glycoconjugated triblock copolymer, **4**. The chromatograms of the product with the polymerization time of above 3 h exhibited small shoulders in the low molecular weight region, hence, the key to preparing **4** with a well-defined structure should be lowering the polymerization time. A possible explanation of this result might be the presence of small amounts of the incomplete TEMPO functionality on one side of the chain ends.

The polymerization of St with **3** was conducted with the [St]/[**3**] of 1000/1 for 2 h to prepare **4** with a higher molecular weight. The SEC chromatogram of the product exhibited one peak with the $M_{w,SEC}$ value of 26,400 and the M_w/M_n of 1.17 (Fig. 2d). Therefore, the glycoconjugated triblock copolymer **4** with a variety of molecular weights should be synthesized through the polymerization condition by increasing not the polymerization time but the [St]/[**3**] value.

Fig. 1b shows the ^{1}H NMR spectrum of **4**. The signals of **4** were similar to those of **3**, except that the integration ratios of the signals due to the St units and the **1** unit for **4** were significantly larger than that for **3**. The compositions (y–x–y) of **4**, which were determined from the integration ratios of the signals due to the St units and the **1** unit, were found to be 20–17–20, 45–17–45, and 100–17–100 for **4-I**, **4-II**, and **4-III**, respectively.

The SLS measurements were performed to determine the absolute weight-average molecular weights ($M_{w,SLS}$) of **4**. The $M_{w,SLS}$ values were 12,500, 17,900, and 29,400 for **4-I**, **4-II**, and **4-III**, respectively. The y–x–y values calculated from the $M_{w,SLS}$ were found to be 19–17–19, 45–17–45, and 100–17–100 for **4-I**, **4-II**, and **4-III**, respectively. These values were in good agreement with those determined from the ^{1}H NMR spectra for **4**. Table 1 summarizes the results of the characterization of **4**.

*3.3. Amphiphilic property of glycoconjugated triblock copolymer **5***

The glycoconjugated triblock copolymers **4** were modified into an amphiphilic polymer by deacetylation using sodium methoxide in dry-THF. Fig. 1c shows the ^{1}H NMR spectrum of the product in DMSO-d_6. The signals due to the

Table 1
Polymerization of styrene (St) with glycoconjugated prepolymer (**3**) to afford glycoconjugated triblock copolymer (**4**)

Sample	[St]/[**3**][a]	Time (h)	Yield (%)	$M_{w,SEC}$[b]	M_w/M_n[b]	$M_{w,SLS}$[c]	d*n*/d*c* (ml g^{-1})	$[\alpha]_D$[d] (deg)	Composition[e] (*y*–*x*–*y*)
3	–	–	–	4600	1.09	8500	0.0187	−49.6	–
4-I	400/1	1	10	7800	1.14	12,500	0.0520	−31.0	20–17–20
4-II	400/1	2	18	10,700	1.12	17,900	0.0727	−24.7	45–17–45
4-III	1000/1	2	17	26,400	1.17	29,400	0.0805	−15.1	100–17–100

[a] Molar ratio of St and **3** in the feed.
[b] Determined by SEC using polystyrene standards.
[c] Determined by SLS measurement.
[d] Measured in $CHCl_3$ at 23 °C (*c* 1.0).
[e] Determined by ^1H NMR spectra.

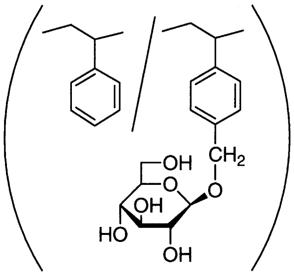
Table 2
Solubility glycoconjugated triblock copolymer **5** (prepared from polymer **4** through deacetylation using NaOMe in THF) and the corresponding statistical copolymer **6**

Sample	f_g (wt%)	Solubility[a]	
		Toluene	H_2O
5-I	30	(−)	(+)
5-II	21	(−)	(−)
5-III	12	(±)	(−)
6-I	32	(−)	(−)
6-II	22	(±)	(−)
6-III	13	(++)	(−)

Cited from Ref. [28].
[a] (−): insoluble, (±): swelled, (+): stably suspended, (++): soluble.

St units (0.7–2.4 and 6.1–7.5 ppm) appeared along with the characteristic signals due to the saccharide residues (2.9–5.5 ppm), whereas the signals due to the acetyl groups (1.8–2.2 ppm) disappeared. Thus, the product was assigned to the triblock copolymer composed of polystyrene and poly(4-vinylbenzyl glucoside), **5**.

Table 2 summarizes the solubility of **5** along with its weight fraction of the glucose residue (f_g, wt%), which was calculated from the composition of the respective **4**. Table 2 shows the solubility of the corresponding statistical copolymer (**6**) (Scheme 2), which has been previously reported [28]. The triblock copolymer **5** (and statistical copolymer **6**) showed various solubility depending on the f_g values. In a good solvent for polystyrene such as toluene, the solubilities of **5** was found to be poorer than that of **6**, though their respective f_g values were very similar. For example, **5-II** was insoluble (−) thus producing a precipitate, while **6-II** swelled (±) giving a gel. In addition, **5-III** swelled (±), while **6-III** was soluble (++) giving a clear solution. A possible explanation for this result may be that the triblock copolymer **5**, i.e. there are multiple hydroxyl groups in the middle of the chain, is likely to self-assemble in a good solvent of polystyrene forming an insoluble three-dimensional network structure. In a good solvent for the saccharide such as H_2O, **5** and **6** were insoluble (−), except that **5-I** was suspended (+) thus producing a turbid aqueous solution. Hence, the solubility of **5** might be higher than that of **6**. The turbid aqueous solution for **5-I** was characterized by the DLS measurements. The formation of the particles with an average diameter of 110 nm was observed, indicating that **5-I** was stably suspended by forming aggregates in H_2O.



6

Scheme 2. Glycoconjugated statistical copolymer **6**.

4. Conclusion

A triblock copolymer composed of polystyrene and poly(4-vinylbenzyl glucoside) was prepared via the 2,2,6,6-tetramethylpiperidiloxy (TEMPO)-mediated living radical polymerization, followed by deacetylation. In the first step, 4-vinylbenzyl glucoside peracetate was polymerized with α,α′-bis(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-1,4-diethylbenzene as an initiator to afford poly(4-vinylbenzyl glucoside peracetate) having TEMPO on both sides of the chain ends, i.e. the glycoconjugated prepolymer. In the second step, styrene was polymerized with a glycoconjugated prepolymer in chlorobenzene. The product was characterized by SEC, SLS measurement, and ^1H NMR spectroscopy, which indicated that the polymerization system successfully afforded the triblock copolymer composed of polystyrene and poly(4-vinylbenzyl glucoside peracetate). The obtained copolymers were modified by deacetylation into the triblock copolymer composed of polystyrene and poly(4-vinylbenzyl glucoside). The solubility of the polymer was examined using a good solvent for polystyrene and a good one for the saccharide.

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