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Glycoconjugated Polymer. 4. Synthesis and Aggregation Property of Well-Defined End-Functionalized Polystyrene with β-Cyclodextrin

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ABSTRACT: 2,2,6,6-Tetramethylpiperidinyloxy (TEMPO)-substituted β-cyclodextrin (β-CyD), **1**, was synthesized as the initiator for the nitroxide-mediated living radical polymerization. Styrene (St) was polymerized with **1** using a molar ratio of St and **1** in a feed ([St]/[**1**]) of 200 at 120 °C for 6 h. The size exclusion chromatography (SEC) trace of the product exhibited a symmetrical peak with a weight-average molecular weight ($M_{\mathrm{w,SEC}}$) of 11 400 and a polydispersity ($M_{\mathrm{w}}/M_{\mathrm{n}}$) of 1.13. In the ^{1}H NMR spectrum of the product, the signals due to polystyrene (PSt) appeared along with the characteristic signals due to the **1** unit. Thus, the product was assignable to the end-functionalized PSt with acetylated β-CyD, **2**. The introduction of acetylated β-CyD into **2** was found to occur in a quantitative fashion, which was confirmed by thin-layer chromatography equipped with a flame ionization detector (TLC-FID). For the [St]/[**1**] of 600 at 120 °C, the St/**1** system proceeded in a controlled manner to afford **2** with polymerization times of 1.5−9 h with yields of 5−40% and $M_{\mathrm{w,SEC}}$'s of 7500−26 000. On the other hand, the St/**1** system for 15 and 20 h afforded polymers with 54 and 75% though an unexpected side reaction occurred. Polymer **2** with $M_{\mathrm{w,SEC}}$'s of 7500−26 000 was modified by deacetylation using sodium methoxide in dry THF into end-functionalized PSt with β-CyD, **3**. Particle formation was observed during dynamic laser light scattering measurements of **3** in benzene, indicating that **3** was stably suspended in a good solvent for PSt by forming aggregates with β-CyD as a core. The average aggregation numbers (N_{A}) of the aggregates were found to range from 42 to 125, which were determined by static laser light scattering measurement.

Introduction

For polymer chemistry, one prime role of saccharides is to modify hydrophobic vinyl polymers into water-soluble and amphiphilic materials,[1] so that much attention has been directed in recent years to the synthesis of well-defined glycoconjugated macromolecular architectures based on a vinyl monomer possessing a saccharide residue, vinyl saccharide. Several research groups reported that glycoconjugated block copolymers have been successfully prepared using living cationic polymerization,[2] living anionic polymerization,[3] atom transfer radical polymerization,[4,5] and nitroxide-mediated living radical polymerization[6,7] of vinyl saccharides. Many of them were found to show amphiphilic properties such as surface activity and a self-assembling property. Recently, we reported that core-glycoconjugated star-shaped polystyrene was synthesized through the coupling reactions of living polymers in the presence of vinyl saccharides and showed encapsulation ability toward water-soluble compounds.[8]

End-functional polymers with saccharide residues are another class of well-defined glycoconjugated architectures. There have been few attempts, however, to synthesize an end-functionalized polymer with saccharides and examine their amphiphilic property; e.g., Hirao et al. reported that end-functionalized polystyrenes with a definite number of monosaccharide residues were prepared by means of living anionic polymerization based on specially designed saccharide-based terminating agents and showed an aggregation property in several organic solvents.[9]

Controlled radical polymerizations using functionalized initiators was shown to be an efficient synthetic method for end-functional polymers due to the limited functional group tolerance.[10] Additionally, large amounts of malto-oligosaccharides including β-cyclodextrin (β-CyD) have been produced from starch as a raw material through enzyme-catalyzed biotransformation in recent years.[11] Hence, an increasingly important theme in polymer chemistry is the synthesis of materials with high functionality using such abundant and economic resources as starting materials. For example, Haddleton and Ohno reported that well-defined oligosaccharide-terminated poly(methacrylate)s were obtained through copper(I)-mediated living radical polymerization using a sugar-based initiator.[12]

In the article, we report the synthesis of end-functionalized polystyrenes (PSt) with a saccharide residue and their aggregation properties in a good solvent for PSt. For the synthetic procedure as illustrated in Scheme 1, we designed and synthesized 2,2,6,6-tetramethylpiperidiloxy (TEMPO)-substituted β-CyD, **1**, as an initiator for the nitroxide-mediated living radical polymerization. Styrene (St) was polymerized with **1** to afford the end-functionalized PSt with an acetylated β-CyD, **2**. In addition, after **2** was deacetylated to produce the end-functionalized PSt with β-CyD, **3**, we examined the aggregation property of **3** in good solvents for the PSt.

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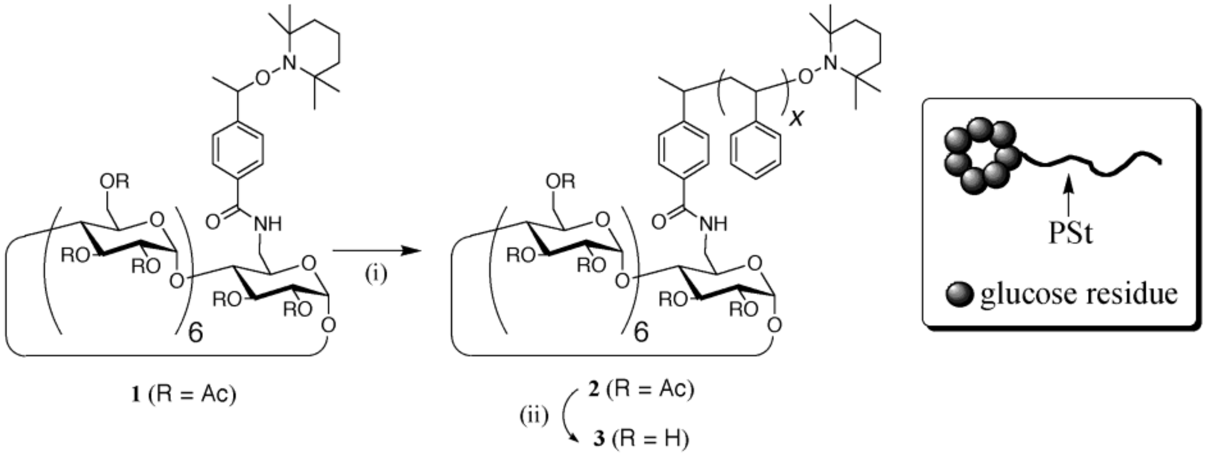
Scheme 1. Procedures: (i) Polymerization of St with 1; (ii) Deacetylation Using NaOMe in THF



Experimental Section

Materials. Dry tetrahydrofuran (THF, >99.5%), dry *N*,*N*-dimethylformamide (DMF, >99.5%), acetic anhydride (Ac_2O, >94.0%), and pyridine (>99.5%) were obtained from Kanto Chemical Co., Japan. Dicyclohexylcarbodiimide (DCC, >95.0%), triethylamine (Et_3N, >99.0%), 4-(dimethylamino)pyridine (DMAP, >99.0%), and 28 wt % sodium methoxide (NaOMe) in methanol were obtained from Wako Pure Chemical Industries, Japan. *N*-Hydroxybenzotriazole (HBT, >95.0%) was obtained from the Tokyo Chemical Industry Co., Japan. These chemicals were used without further purification. Styrene (St) (Kanto Chemical Co., Japan, >99.0%) was distilled prior to use. Methyl-4-[1′-(2″,2″,6″,6″-tetramethyl-1″-piperidinyloxy)-ethyl]benzoic acid[13] and 6-amino-6-deoxy-β-cyclodextrin[14] were prepared according to literature procedures.

Measurements. The ^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-GX270 and JEOL JNM-A400II instruments. Mass spectroscopy (MS) was recorded on JEOL JMS-SX102A and JEOL JMS-AX500 (GC-MS and NMR Laboratory, Faculty of Agriculture, Hokkaido University). Optical rotations were measured using a Jasco DIP-1000 digital polarimeter. The size exclusion chromatography (SEC) was performed at 40 °C in chloroform (1.0 mL min^{-1}) using a Jasco GPC-900 system equipped with a Waters Ultrastyragel 7 mm column (linear, 7.8 mm × 300 mm) and a Shodex KF-804L column (linear, 8 mm × 300 mm). The weight-average molecular weight ($M_{w,SEC}$) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. TLC-FID measurements were performed using an Iatron Laboratories IATRON MK-5 with toluene/hexane (4/1) as the mobile phase. The preparative SEC was performed at 23 °C in chloroform (3.8 mL min^{-1}) using a JAI LC-908 system equipped with two JAI JAIGEL-3H (20 mm × 600 mm) and a JAI JAIGEL-5H (20 mm × 600 mm) polystyrene columns and JAI UV-310 and JAI RI-5HC detectors. The static laser light scattering (SLS) measurement was performed at 25 °C on an Otsuka Electronics DLS-7000 light scattering spectrophotometer ($\lambda = 633$ nm; four-point measurements). The refractive index increment (dn/dc) was measured 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 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.

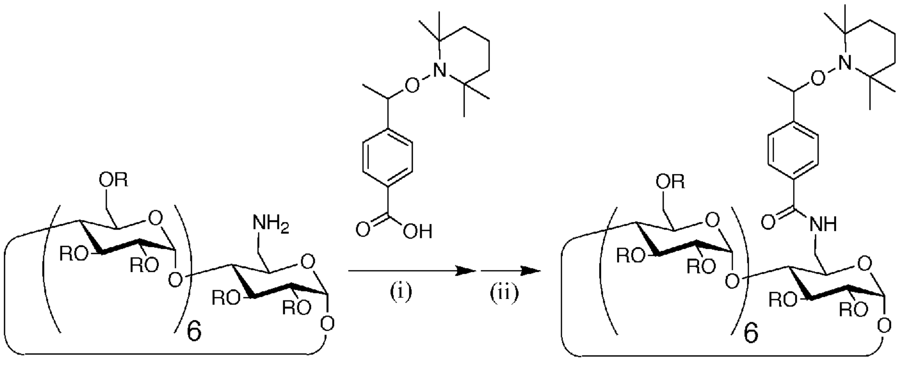
4-[1′-(2″,2″,6″,6″-Tetramethyl-1″-piperidinyloxy)ethyl]-benzoic Acid. To a solution of methyl 4-[1′-(2″,2″,6″,6″-tetramethyl-1″-piperidinyloxy)ethyl]benzoic acid (16 g, 47 mmol) in ethanol (100 mL) was added aqueous potassium hydroxide (33 mL of a 4 N solution), and the solution was heated at 40 °C for 8 h. Then 2 N HCl solution (65 mL) was added to the solution in an ice bath. The solution was evaporated to remove ethanol and extracted with chloroform (2 × 100 mL). The combined organic layers were washed with several portions of water, dried with anhydrous $MgSO_4$, and evaporated to dryness to give acid derivatives as a white solid. The product was used without further purification in the next step. Yield: 13 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.07 (d, $J = 8.3$ Hz, 2H, Ar H), 7.42 (d, $J = 8.3$ Hz, 2H, Ar), 4.86 (q, $J = 7.0$ Hz, 1H, $-CHCH_3$), 1.48 (d, $J = 6.8$ Hz, 3H, $-CHCH_3$), 1.45 (br, 6H, $-CH_2-$), 1.30, 1.18, 1.03, 0.64 (each br s, 12H, $-CH_3$). ^{13}C NMR (100.4 MHz, $CDCl_3$, δ): 171.9, 145.7, 130.1, 127.8, 126.5, 82.9, 59.8, 40.2, 34.3, 30.4, 23.6, 20.3, 17.1. IR (KBr, cm^{-1}): 2942, 1682, 1376. Anal. Calcd for $C_{18}H_{27}NO_3$: C, 70.79; H, 8.91; N, 4.59. Found: C, 70.52; H, 8.86; N, 4.54.

Mono-6-[4-(1′-(2″,2″,6″,6″-tetramethyl-1″-piperidinyloxy)-ethyl)benzamido]per-2,3,6-acetyl-β-cyclodextrin (1). To a solution of 4-[1′-(2″,2″,6″,6″-tetramethyl-1″-piperidinyloxy)-ethyl]benzoic acid (2.8 g, 9.0 mmol) and HBT (1.4 g, 11 mmol) in dry DMF (100 mL) was added DCC (1.9 g, 9.3 mmol) with stirring at 0 °C. After stirring at 0 °C for 1 h, a white precipitate of dicyclohexylurea was observed. To the heterogeneous solution was added a suspension of 6-amino-6-deoxy-β-cyclodextrin (7.2 g, 6.4 mmol) and Et_3N (0.93 g, 9.2 mmol) in dry DMF (150 mL). After stirring at room temperature for 20 h, the mixture was evaporated in vacuo. To the residue was added hexane (ca. 30 mL), and the precipitates were filtered, washed with several portions of hexane, and dried in vacuo to afford a pale yellow solid. Yield: 12 g.

The solid (6.0 g) was dissolved in dry pyridine (38 mL), and then Ac_2O (25 mL) and a catalytic amount of DMAP were added at 0 °C. After stirring at room temperature for 5 days, the reaction mixture was added to ethanol (20 mL) at 0 °C. The mixture was evaporated in vacuo and redissolved in chloroform (150 mL). The chloroform solution was washed with 1 N HCl aqueous solution (50 mL), water (50 mL), 1 N NaOH aqueous solution (50 mL), water (50 mL), and saturated NaCl solution (50 mL), dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (1/9, v/v) to give initiator **1** as a white solid. Yield: 5.1 g (72% from 6-amino-6-deoxy-β-cyclodextrin). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.78 (d, $J = 8.4$ Hz, 2H, Ar H), 7.38 (d, $J = 7.8$ Hz, 2H, Ar), 6.82 (br s, 7H, $-NH$), 5.37−4.12 (m, 43H, H-1 + H-5 + H-4 + $-CHCH_3$ + H3 + H-6), 3.59−3.83 (m, 7H, H-2), 2.17−1.97 (each s, 60H, $-COCH_3$), 1.46 (d, $J = 6.5$ Hz, 3H, $-CHCH_3$), 1.43−1.24 (m, 6H, $-CH_2-$), 1.29, 1.16, 1.01, 0.65 (each br s, 12H, $-CH_3$). ^{13}C NMR (67.8 MHz, $CDCl_3$, d): 170.9−169.2, 167.4, 149.6, 132.4, 128.3, 127.1, 126.5, 97.1, 96.8, 96.5, 82.8, 77.2, 71.0−69.5, 62.9, 62.5, 59.6, 40.2, 34.3, 23.5, 20.7, 20.3, 17.1. IR (KBr, cm^{-1}): 3424, 1764, 1665. $[\alpha]^{23}_D = +94.4°$ (c 1.0, $CHCl_3$). Anal. Calcd for $C_{100}H_{136}N_2O_{56}$: C, 53.09; H, 6.06; N, 1.24. Found: C, 53.30; H, 6.12; N, 1.25.

Polymerization. Initiator **1** (1.1 g, 0.50 μmol) was dissolved in St (10 g, 100 mmol). Oxygen was removed 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 mixture was

Scheme 2. Synthesis of 1: (i) Coupling Reaction Using DCC in DMF in the Presence of HBT and Et_3N; (ii) Acetylation Using Ac_2O in Pyridine



R = H

1 (R = Ac)

then stirred at 120 °C for 6 h. After cooling in liquid nitrogen, the mixture was diluted with chloroform (ca. 22 mL) and then poured into methanol (ca. 1 L). The precipitate was filtered off and purified by reprecipitation with chloroform−methanol and dried in vacuo to give polymer **2** as a white powder. Yield: 5.4 g (43%). $M_{w,SEC} = 1.14 \times 10^4$, $M_w/M_n = 1.13$. $M_{w,SLS} = 1.24 \times 10^4$. $[\alpha]^{23}_D = +18.1°$ (*c* 1.0, $CHCl_3$).

Deacetylation. To a solution of polymer **2** (2.73 g, $M_{w,SLS} = 1.24 \times 10^4$) in dry THF (25.0 mL) was added catalytic amounts (ca. 5 drops) of 28 wt % NaOMe in methanol with cooling. After stirring for 3 days at room temperature, the mixture was poured into methanol/water (9/1, v/v, ca. 500 mL). The precipitate was filtered off, washed with water and then methanol, and finally purified by reprecipitation from chloroform−methanol twice to yield polymer **3**. Yield: 2.5 g (99%).

Results and Discussion

Synthesis of Initiator 1. 4-[1′-(2″,2″,6″,6″-Tetramethyl-1″-piperidinyloxy)ethyl]benzoic acid was coupled with mono-6-deoxy-6-amino-*β*-cyclodextrin using dicyclohexylcarbodiimide (DCC) in DMF, as shown in Scheme 2. To couple the carboxylic acid exhaustively with the amino groups, the reaction was performed in the presence of *N*-hydroxybenzotriazole (HBT) and triethylamine (Et_3N).[15] The crude residue was treated with acetic anhydride (Ac_2O), followed by purification with column chromatography to give a product which was soluble in common organic solvents. The analytical data indicated that the product was assignable to mono-6-[4-(1′-(2″,2″,6″,6″-tetramethyl-1″-piperidinyloxy)ethyl)-benzamido]per-2,3,6-acetyl-*β*-cyclodextrin, **1**. Figure 1A shows the ^1H NMR spectrum of **1**.

Synthesis and Characterization of End-Functionalized PSt with Acetylated *β*-CyD, 2. Styrene (St) was polymerized with **1** using a molar ratio of St and **1** in the feed ([St]/[**1**]) of 200 at 120 °C. The polymerization for 6 h afforded a product in a 43% yield, which was based on the consumption of St. Figure 2 shows a size exclusion chromatography (SEC) trace of the product, which exhibited a symmetrical peak with a weight-average molecular weight ($M_{w,SEC}$) of 11 400 and a polydispersity (M_w/M_n) of 1.13. For the ^1H NMR spectrum of the product (Figure 2B), the signals due to polystyrene (PSt) appeared at 1.0−2.0 and 6.2−7.4 ppm along with the characteristic signals due to **1** at 0.1−1.2 ppm (the methyl protons in the TEMPO moiety) and 3.4−5.4 ppm (the methine and methylene protons in the acetylated *β*-CyD moiety). The SEC and ^1H NMR analyses indicated that the product was assignable to the PSt initiated by **1**, i.e., the end-functionalized PSt with acetylated *β*-CyD, **2**.

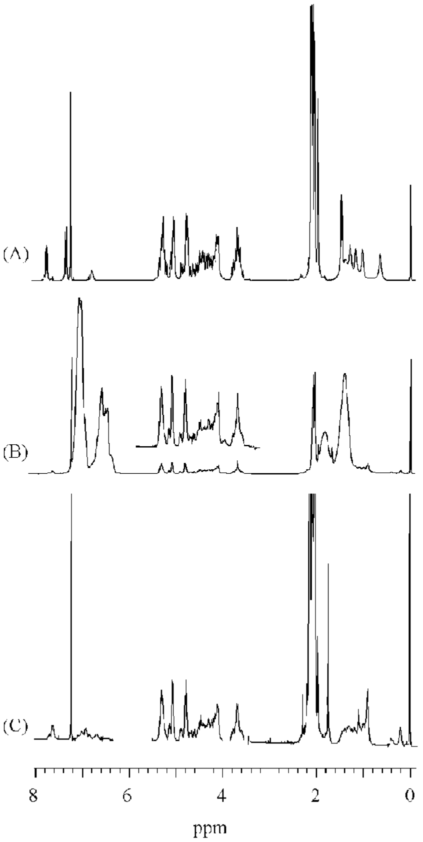


Figure 1. ^1H NMR spectra in $CDCl_3$ of (A) **1**, (B) **2** obtained though the polymerization of St with **1** using an [St]/[**1**] of 200 for 6 h, and (C) **6** obtained though the polymerization of St-d_8 with **1** using an [St-d_8]/[**1**] of 120 for 24 h, followed by purification using preparative SEC.

It is well-known that the polymerization of St using 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-ethane, initiator **4**, proceeded in a controlled manner to produce PSt. Hence, as a control, we polymerized St using **4** ([St]/[**1**] = 200, 120 °C, 6 h) as shown in Scheme 3. The polymerization afforded PSt **5** (yield = 45%, $M_{w,SEC} = 10\ 000$, $M_w/M_n = 1.09$).[8] Although the yield of **2** was found to be very similar to that of **5**, the $M_{w,SEC}$ of **2** was slightly larger than that of **5**. This result suggested that the hydrodynamic volume of **2** was larger than that of **5** due to the presence of the bulky acetylated *β*-CyD moiety.

The degree of end-functionality with acetylated *β*-CyD, f_{end}, had to be determined for **2**. Using a thin-layer

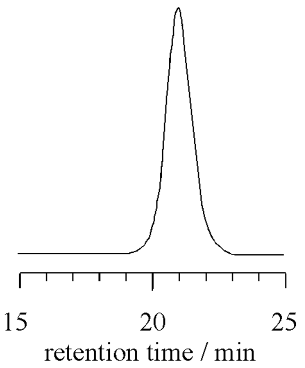


Figure 2. SEC trace of **2** obtained though the polymerizations of St with **1** using an [St]/[**1**] of 200 for 6 h.

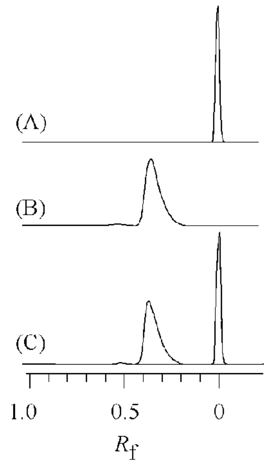
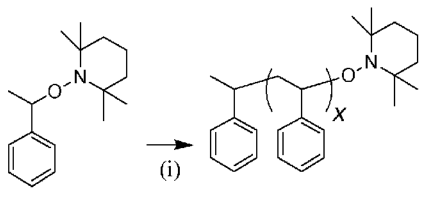


Figure 3. TLC-FID traces of **2** and **5**, which were obtained though the polymerizations of St with **1** and **4**, respectively, using an [St]/[initiator] of 200 for 6 h: (A) **2**, (B) **5**, and (C) **2** + **5**.

Scheme 3. Synthesis of 5: (i) Polymerization of St with 4 with an [St]/[4] of 200/1 at 120 °C for 6 h



4 **5**

Table 1. Polymerization of St[a]

initiator	product	yield[b] (%)	$M_{w,SEC} \times 10^{-4}$ [c]	M_w/M_n [c]	R_f [d]
1	**2**	43	1.14	1.13	0
4	**5**	45	1.00	1.09	0.37

[a] Performed with an [St]/[initiator] of 200 at 120 °C for 6 h. [b] Based on the consumption of St. [c] Determined by SEC using polystyrene standards. [d] Determined by TLC-FID analysis.

Table 2. Synthesis and Characterization of 2 and Aggregation Property of 3

		2[a]			**3**[b]	
time (h)	yield[c] (%)	$M_{w,SEC}$ [d] $\times 10^{-4}$	M_w/M_n [d]	$M_{w,SLS}$ [f] $\times 10^{-4}$	$M_{w,SLS}$ [f] $\times 10^{-4}$	N_A
1.5	5.0	0.75	1.27	0.99	123	125
3	22	1.68	1.15	2.26	170	75
6	25	1.94	1.14	2.62	136	52
9	40	2.60	1.09	3.20	134	42
15	54	3.11[e]	1.43[e]			
20	75	3.66[e]	1.25[e]			

[a] Prepared through the polymerization of St with **1** with an [St]/[**1**] of 600 at 120 °C. [b] Prepared through deacetylation of **2**. [c] Based on the consumption of St. [d] Determined by SEC using polystyrene standards. [e] A byproduct with high molecular weight was formed as shown in Figure 4. [f] Determined by SLS measurement.

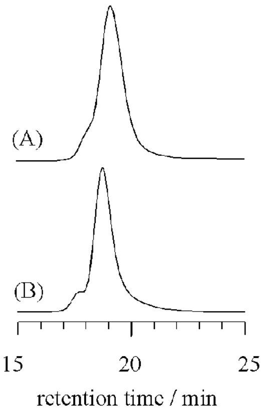


Figure 4. SEC traces of the product obtained though the polymerization of St with **1** using an [St]/[**1**] of 600 for (A) 15 h and (B) 20 h.

chromatograph equipped with a flame ionization detector (TLC-FID) is one convenient method to estimate the f_{end} value.[9] Figure 3 shows the TLC-FID traces of **2** and **5** (toluene/hexane = 4/1). In the TLC-FID trace of **5** one peak appeared with an R_f value of 0.37, while that of **2** appeared near the spotting point. Hence, the introduction of acetylated β-CyD into **2** was found to occur in a quantitative fashion.

St was polymerized with **1** using an [St]/[**1**] of 600 at 120 °C to afford products (Table 2). The SEC traces of the products exhibited one symmetrical peak with a polymerization time of 1.5−9 h. The yields and $M_{w,SEC}$'s of the products increased from 5.0 to 40% and from 7500 to 26 000, respectively, with increasing polymerization time, while the M_w/M_n's were low values below 1.27. Thus, under these conditions, the St/**1** system proceeded in a controlled manner. The ^{1}H NMR and TLC-FID analyses indicated that the products were assignable to polymer **2** with an f_{end} value of ca. 1.0.

On the other hand, when the polymerizations were performed for a longer time, e.g., 15 and 20 h (Table 2), the SEC traces of the products exhibited a main peak along with a small shoulder in the higher molecular weight regions, as shown in Figure 4. The main product and the byproduct, which were fractionated using preparative SEC, respectively, were characterized by ^{1}H NMR spectroscopy. However, there was no significant difference in the spectra between the main product and the byproduct. Furthermore, the peak top of the SEC traces of the main product and the byproduct, which were obtained though the polymerization for 20 h, were corresponding to the M_w values of 35 800 and 66 000, respectively (Figure 4B). Hence, the byproduct might be the dimer of the main product. Although further characterizations were not performed for the byproduct, it is important to note that the key to preparing **2** with a well-defined structure might be lowering their yields below about 40%.

Styrene-d_8 was polymerized using **1** with a [St-d_8]/[**1**] of 120 at 120 °C for 24 h to afford the product in a 62% yield. The SEC trace of the product exhibited a small shoulder in the higher molecular weight region. The main product was fractionated using preparative SEC to afford polymer **6** (yield of the fractionation =

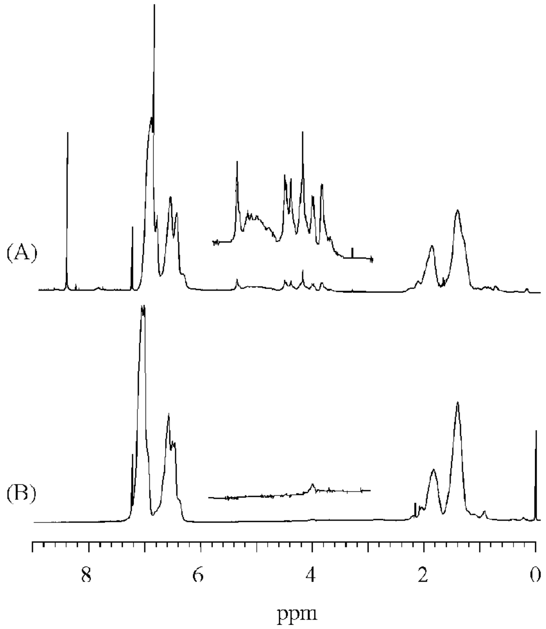


Figure 5. ^{1}H NMR spectra of **3** (A) in pyridine-d_5 and (B) in $CDCl_3$.

91%, $M_{w,SEC} = 8000$, $M_w/M_n = 1.14$). As shown in Figure 1C, the signal due to the acetylated β-CyD units (3.4−5.4 ppm) of **6** was quite similar to that of **1**. Therefore, the acetylated β-CyD moiety due to the **1** unit was not cleaved after the polymerization.

Aggregation Property of End-Functionalized PSt with β-CyD, 3. Polymer **2** was deacetylated using sodium methoxide in dry THF. For the ^{1}H NMR spectrum of the product in pyridine-d_5 (Figure 5A), the signals due to PSt (1.0−2.0 and 6.2−7.4 ppm) appeared along with the characteristic signals due to the β-CyD (3.4−5.4 ppm), whereas the signals due to the acetyl groups disappeared. Thus, the product was assigned to the end-functionalized PSt with β-CyD, **3**.

It was found that **3** showed characteristic properties in solvents which were good solvents for PSt but poor solvents for β-CyD. For laser light scattering (LS) measurements, as an example, the scattering intensity of **3** was significantly strong compared to that of **2**. Particle formation was observed for **3** in benzene using a dynamic laser light scattering (DLS) measurement. The average diameter of the particles ranged from ca. 20 to 43 nm, which was determined by cumulant analysis. In addition, for the ^{1}H NMR spectrum of **3** in $CDCl_3$, the signals due to the β-CyD were extremely broadened and disappeared as shown in Figure 5B, indicating that the intramolecular mobility of the protons in the β-CyD moieties of **3** was significantly eliminated in this poor solvent ($CDCl_3$). These results indicated that polymer **3** was stably suspended in a good solvent for PSt by forming aggregates with β-CyD as a core.

The static laser light scattering (SLS) measurement was performed to determine directly the average molar mass, $M_{w,SLS}$, of the aggregates. As summarized in Table 2, the $M_{w,SLS}$ of the aggregates ranged from 1.23×10^6 to 1.70×10^6. The average aggregation numbers (N_A) of **3** should be calculated from the $M_{w,SLS}$ of the aggregates divided by that of the corresponding $M_{w,SLS}$ of **2**. The N_A of **3** in the aggregates was found to range from 42 to 125. Therefore, the β-CyD moiety in **3** acted as a very efficient unit to form aggregates with a high N_A value in a good solvent for PSt.

Conclusions

β-CyD was modified into the initiator (**1**) for the TEMPO-mediated living radical polymerization. The polymerization of St with **1** successfully produced the end-functionalized PSt with acetylated β-CyD, **2**. The end-functionalized PSt with β-CyD (**3**), which was obtained by deacetylation of **2**, was stably suspended in a good solvent for PSt by forming aggregates with β-CyD as a core. The average aggregation numbers (N_A) of **3** ranged from 42 to 125. Thus, initiator **1** was found to be a useful tool for constructing end-functional PSt with an excellent hydrophilic property to form aggregates with a high N_A value.

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