Glycoconjugated Polymer. 5. Synthesis and Characterization of a Seven-Arm Star Polystyrene with a β-Cyclodextrin Core Based on TEMPO-Mediated Living Radical Polymerization

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ABSTRACT: β-Cyclodextrin (β-CyD) was modified into a seven-functional initiator (**1**) for 2,2,6,6-tetramethylpiperidinyloxy- (TEMPO-) mediated living radical polymerization. Styrene (St) was polymerized with **1** under several conditions to afford original products **I**−**IV**. Size exclusion chromatography (SEC) traces of **I**−**IV** exhibited trimodal molecular weight distributions; hence, they were fractionated into the respective three species, i.e., main products **2**, byproducts **3** with lower molecular weights, and byproducts **4** with higher molecular weights. The weight-average molecular weights determined by SEC and static laser light scattering measurement ($M_{w,SEC}$ and $M_{w,SLS}$, respectively) were 1.34×10^4 and 2.98×10^4 for **2-I**, 4.52×10^4 and 6.77×10^4 for **2-II**, 1.35×10^5 and 1.87×10^5 for **2-III**, and 9.67×10^5 and 1.89×10^6 for **2-IV**. The $M_{w,SLS}$'s were larger than the respective $M_{w,SEC}$'s. In the ^{1}H NMR spectra of **2**, the signals due to polystyrene (PSt) appeared along with the characteristic signals due to the **1** unit. Therefore, those of **2** were assignable to a star PSt with an acetylated β-CyD core. Polymer **2** was treated with sulfuric acid to give core-cleaved polymer **2′**. The $M_{w,SEC}$'s were 2.80×10^3, 9.60×10^3, 2.70×10^4, and 2.61×10^5 for **2′-I**, **2′-II**, **2′-III**, and **2′-IV**, indicating that the arm number of **2**, N_{PSt}, was seven. The byproducts **3** and **4** were characterized and found to be a TEMPO-terminated linear PSt and a star−star coupled polymer, respectively. The seven-arm star PSt with a β-CyD core, **5**, was obtained through deacetylation of **2** using sodium methoxide in dry THF. The $M_{w,SLS}$ values were 3.96×10^5, 3.78×10^5, 2.40×10^5, and 1.94×10^6 for **5-I**, **5-II**, **5-III**, and **5-IV**. Hence, **5-I** and **5-II** showed aggregation in a good solvent for PSt with aggregation-numbers (N_A) of 13 and 6, respectively.

Introduction

Star polymers are branched polymers consisting of several linear arms linked to a central core.[1,2] In the field of star polymer synthesis, one prime interest for many researchers is to achieve a high degree of control over arm polymers through precise synthetic techniques involving living anionic[1−3] and cationic polymerization.[2,4] For example, Roovers et al. reported that star polymers constituted of 64 and 128 arms were synthesized by deactivation of a linear living anionic polymer onto a dendritic molecule containing 64 and 128 chlorosilane functions.[3b] Hirao et al. reported that hetero-arm star polymers with a precise arm number were synthesized by an iterative approach based on living anionic polymerization using 1,1-diphenylene derivatives.[3c] Fukui et al. reported that multiarmed polymers were synthesized using multifunctional coupling agents for living cationic polymers.[4a] Jacob et al. reported that star polymers constituted of eight arms were synthesized through living cationic polymerization of isobutylene using calixarene as a multifunctional initiator.[4b]

Controlled radical polymerizations[5] have been interestingly developed and applied to the synthesis of well-defined star polymers with a precise arm number using a multifunctional initiator. Several research groups reported that well-defined star polymers were synthesized through atom transfer radical polymerization (ATRP) using multihalides.[6] Stenzel-Rosenbaum et al. reported that star polymers constituted of six arms were synthesized through reversible addition−fragmentation transfer (RAFT) using a hexafunctional RAFT agent.[7] For nitroxide-controlled radical polymerization, Hawker reported that a trifunctional 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) adduct provided a three-arm polystyrene.[8]

Another interest in the field of star polymer synthesis is to introduce functional groups into the core, i.e, a synthesis of core-functionalized star polymers. To synthesize such polymers, cross-linking reactions of preformed living polymers have been performed using a divinyl compound. Kanaoka et al. reported that a star polymer whose microgel core carries hydroxyl groups was prepared on the basis of living cationic polymerization.[9] In our laboratory, a core-glycoconjugated star polymer was synthesized via the cross-linking reaction of TEMPO-terminated polystyrene using divinylbenzene in the presence of 4-vinyl glycoside peracetate, followed by deacetylation.[10] Baek et al. reported that a core-functionalized star polymer was synthesized by the linking reaction between living poly(methyl methacrylate) and various functionalized divinyl compounds in the Ru(II)-catalyzed living radical polymerization.[11] There have been few attempts, however, to synthesize a core-functionalized star polymer via polymerization with a multifunctional initiator.

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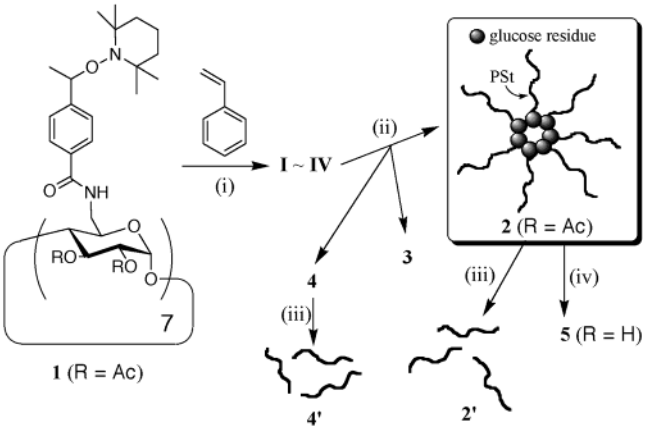
Scheme 1. Procedures[a]



[a] Key: (i) polymerization of St with **1**; (ii) fractionation using preparative SEC; (iii) acid hydrolysis; (iv) deacetylation.

The radical process has the potential of being compatible with a wide variety of functional groups. Thus, it is of interest to extend controlled radical polymerization to the synthesis of a core-functionalized well-defined star polymer using a multifunctional initiator based on an appropriate molecule. We report here the synthesis of a star polymer with seven arms via TEMPO-mediated radical polymerization using a multifunctional initiator based on β-cyclodextrin (β-CyD). Cyclodextrins should be a suitable core-molecule, because they are well-defined cyclic molecules with multiple hydroxyl groups. Indeed, Ohno et al. reported that a 21-arm star polymer having a β-CyD core was synthesized through the ATRP technique.[6f] The total procedure in this paper is illustrated in Scheme 1. We synthesized acetylated β-CyD bonded with TEMPO adducts at C-6 positions, initiator **1**. Styrene (St) was polymerized with the initiator **1** to afford original products with trimodal molecular weight distributions. We fractionated the original product into three species, i.e., star polymer **2**, byproduct **3** with a lower molecular weight, and byproduct **4** with a higher molecular weight. In the article, the characterizations of the respective species are discussed. Furthermore, the star polymer **2** was modified into star polymer **5** by deacetylation. The star polymer **5** possesses a characteristic structure; i.e., a total of 14 hydroxyl groups at the C-2 and C-3 positions of the β-CyD are located on the opposite side to seven polystyrene arms at the C-6 positions. We report herein an aggregation property of **5** in a good solvent for polystyrene.

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.. 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. *N*-Hydroxybenzotriazole (HBT, >95.0%) was obtained from Tokyo Chemical Industry Co.. These chemicals were used without further purification. Styrene (St) (Kanto Chemical Co., >99.0%) was distilled prior to use. Chlorobenzene (Kanto Chemical Co., >99.5%) was distilled over CaH_2 prior to use. A seamless cellulose tube (UC24-32-100) was obtained from Viskase Sales Co. Methyl 4-[1′-(2″,2″,6″,6″-tetramethyl-1″-piperidinyloxy)ethyl]benzoic acid[12] and per-6-amino-β-cyclodextrin[13] were prepared according to literature procedures.

Measurements. The ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-GX270 and a JEOL JNM-A400II instruments. Mass spectroscopy (MS) was recorded on JEOL JMS-SX102A and JEOL JMS-AX500 (GC-MS & NMR Laboratory, Faculty of Agriculture, Hokkaido University) instruments. 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 two Shodex KF-804L columns (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. 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 in toluene at 25 °C on an Otsuka Electronics DLS-7000 light scattering spectrophotometer (λ = 633 nm; four-point measurements). The refractive index increment (dn/dc) was measured in toluene at 25 °C on an Otsuka Electronics DRM-1021 double beam-differential refractometer (λ = 633 nm). Intrinsic viscosities ([η]) were measured by Ubbelohde in benzene at 25 °C.

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. A 2 N HCl solution (65 mL) was then 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, −C*H*CH$_3$), 1.48 (d, J = 6.8 Hz, 3H, −CHC*H*$_3$), 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.

Per-6-[4-(1′-(2″,2″,6″,6″-tetramethyl-1″-piperidinyloxy)-ethyl)benzamido]per-2,3-acetyl-β-cyclodextrin (1). To a solution of 4-[1′-(2″,2″,6″,6″-tetramethyl-1″-piperidinyloxy)-ethyl]benzoic acid (7.0 g, 23 mmol) and 1-hydroxybenzotriazole (HBT) (3.7 g, 28 mmol) in dry DMF (140 mL) was added dicyclohexylcarbodiimide (DCC) (5.7 g, 28 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 per-6-amino-β-cyclodextrin (2.6 g, 2.3 mmol) and triethylamine (1.7 g, 17 mmol) in dry DMF (140 mL). After the mixture was stirred at room temperature for 20 h, precipitated urea was removed by filtration, and the filtrate was evaporated in vacuo. The residue was dissolved in pyridine (20 mL) and then acetic anhydride (23 g, 0.23 mol) was added at 0 °C. After being stirred at room temperature for 20 h, the reaction mixture was poured into ice/water and extracted three times with chloroform. The combined organic phases were washed several times with 1 N HCl, saturated $NaHCO_3$, and NaCl solutions, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography on silica gel with dichloromethane/methanol (40/1, v/v) to give **1** as a white solid. Yield: 5.4 g (63%). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.88 (br s, 7H, NH−), 7.83 (d, J = 7.3 Hz, 14H, Ar H), 7.21 (d, J = 7.8 Hz, 14H, Ar H), 5.21−5.15 (m, 14H, H-1 + H-5), 4.96 (dd, J = 7.8 Hz, 7H, H-4), 4.72 (q, J = 6.5 Hz, 7H, −C*H*CH$_3$), 4.23 (br d, J = 8.6 Hz, 7H, H-3), 4.02 (br s, 14H, H-6), 3.65 (dd, J = 8.9 Hz, 7H, H-2), 2.13 (s, 21H, −COCH$_3$), 1.92 (s, 21H, −COCH$_3$), 1.45 (br s, 21H, −CHC*H*$_3$-), 1.43−1.24 (m, 42H, −CH$_2$−), 1.24, 1.12, 0.97, 0.60 (each br s, 84H, −CH$_3$).^{13}C NMR (67.8 MHz, $CDCl_3$, δ): 170.5, 169.4, 168.1, 149.4, 132.4, 127.4, 126.3, 126.4, 97.3, 82.9, 79.2,

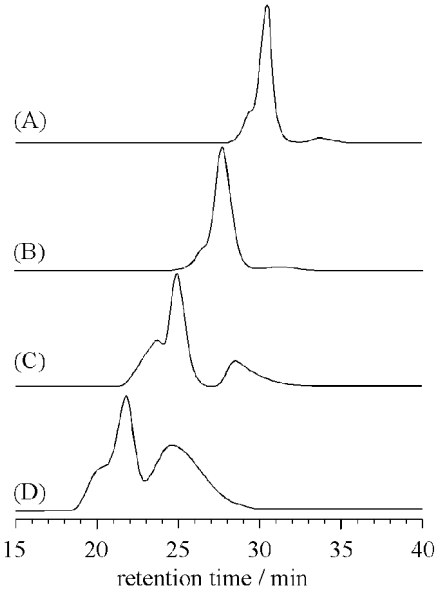


Figure 1. SEC traces of (A) **I**, (B) **II**, (C) **III**, and (D) **IV**.

77.2, 71.1, 70.4, 68.8, 59.6, 40.3, 34.3, 23.6, 20.6, 20.3, 17,1. IR (KBr, cm^{-1}): 3380, 1756, 1656. $[\alpha]^{23}_D = +39.6°$ (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{196}H_{280}N_{14}O_{56}$: C, 63.14; H, 7.57; N, 5.26. Found: C, 62.83; H, 7.50; N, 4.95.

Polymerization. St was polymerized with initiator **1** for the preparation of original products **I**−**IV**. An example of the procedure is described for original product **II**. Styrene (20 g, 0.19 mol) and initiator **1** (98 mg, 26 mmol) were dissolved in chlorobenzene (36 mL). 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 polymerization mixture was then stirred at 125 °C for 2.5 h. After cooling in liquid nitrogen, the mixture was diluted with chloroform (ca. 30 mL) and then poured into methanol (ca. 500 mL). The precipitate was filtered off and purified by reprecipitation with chloroform−methanol and dried in vacuo to give original product **II** as a white powder. Yield: 2.1 g (11%). The SEC chromatogram of **II** exhibited a main peak (26.5−29.5 min) along with small peaks in both high and low molecular weight regions (24.0−26.5 min and 30.5−34.0 min, respectively) as shown in Figure 1B.

Fractionation Using Preparative SEC. The original products **I**−**IV** were fractionated into three parts using preparative SEC. An example of the procedure is described for the original product **II**. The original product **II** (2.0 g) was dissolved in chloroform (8.0 mL) and applied to preparative SEC. The chromatogram of the eluents exhibited a main peak (35.5−47.5 min) along with small peaks in both lower and higher molecular weight regions (30.5−34.0 min and 24.0−26.5 min, respectively). The respective eluents were fractionated, evaporated, redissolved in a small amount of chloroform, and then poured into methanol. The respective precipitates were filtered off and dried in vacuo to give white powders. The yields and the characterization of the respective products are described in the following sections.

Star Polymer 2. An example of the procedure is described for the preparation of star polymer **2-II**. The eluents due to the peak of the SEC chromatogram (26.5−29.5 min) for the original product **II** were fractionated using preparative SEC as above to give star polymer **2-II**. Yield: 1.6 g (82% from the original product **II**). The SEC trace of **2-II** is shown in Figure 2A. $M_{w,SEC} = 4.52 \times 10^4$, $M_w/M_n = 1.05$. $M_{w,SLS} = 6.77 \times 10^4$, $dn/dc = 0.1374$ mL·g^{-1}. $[\eta] = 0.236$ dL·g^{-1}. $[\alpha]^{23}_D = +2.1°$ (*c* 1.0, $CHCl_3$).

Core-Cleaved Polymers 2′. Acid hydrolysis of the β-CyD moiety in star polymer **2** was performed to determine its arm number. An example of the procedure is described for the preparation of core-cleaved polymer **2′-II**: To a stirred solution of star polymer **2-II** (50 mg) in dry THF (2 mL) was slowly added concentrated sulfuric acid (0.45 g, 4.6 mmol). After the reaction was stirred at 60 °C for 2 days, the color of the solution became dark. The whole solution was poured into ice-cooled $NaHCO_3$ solution (3 g/100 mL) and extracted twice with chloroform. The combined organic phases were washed several times with saturated $NaHCO_3$ and NaCl solutions, dried over anhydrous $MgSO_4$, and evaporated to dryness. The obtained polymer was purified by reprecipitation with chloroform−methanol and dried in vacuo to give core-cleaved polymer **2′-II** as a pale yellow powder. Yield: 0.37 g (74%). $M_{w,SEC} = 9.60 \times 10^3$, $M_w/M_n = 1.21$.

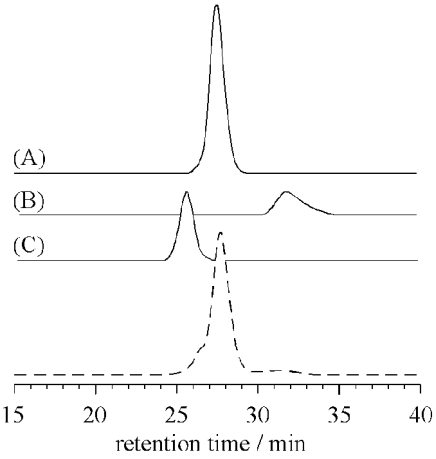


Figure 2. SEC traces of (A) **2-II**, (B) **3-II**, and (C) **4-II**, which were prepared through fractionations of **II** (shown as broken line).

Byproduct 3. An example of the procedure is described for the preparation of byproducts **3-II**. The eluent due to the small peak of the SEC chromatogram (30.5−34.0 min) for the original product **II** were fractionated using the preparative SEC as above to give byproduct **3-II** in trace yield. The SEC trace of **3-II** is shown in Figure 2B. $M_{w,SEC} = 6.90 \times 10^3$, $M_w/M_n = 1.17$.

Byproduct 4. An example of the procedure is described for the preparation of byproduct **4-II**: The eluent due to the small peak of the SEC chromatogram (24.0−26.5 min) for the original product **II** was fractionated using the preparative SEC as above to give byproduct **4-II**. The SEC trace of **4-II** is shown in Figure 2C. Yield: 0.19 g (1.0% from the original product **II**). $M_{w,SEC} = 1.05 \times 10^5$, $M_w/M_n = 1.05$. $M_{w,SLS} = 1.20 \times 10^6$, $dn/dc = 0.1170$ mL·g^{-1}.

Star Polymer 5. Star polymer **2** was modified by deacetylation into star polymer **5**. An example of the procedure is described for the preparation of star polymer **5-II**. To a solution of **2-II** (0.25 g) in dry THF (5.0 mL) was added three drops of 28 wt % sodium methoxide in MeOH. After being stirred for 24 h at room temperature, the mixture was poured into H_2O (ca. 50 mL), then transferred to a cellulose tube, and dialyzed for 2 days with H_2O. The aqueous suspension was freeze-dried to yield star polymer **5-II** as a white powder. Yield: 0.22 g (88%). $M_{w,SLS} = 3.78 \times 10^5$, $dn/dc = 0.1048$ mL·g^{-1}.

Results and Discussion

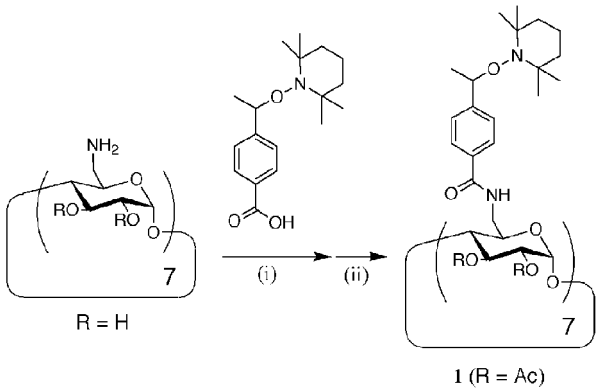
Synthesis of Initiator 1. As shown in Scheme 2, 4-[1′-(2″,2″,6″,6″-tetramethyl-1″-piperidinyloxy)ethyl]-benzoic acid was coupled with per-6-amino-β-cyclodextrin using dicyclohexylcarbodiimide (DCC) in DMF. The reaction was performed in the presence of *N*-hydroxybenzotriazole (HBT) and triethylamine in order to couple carboxylic acid exhaustively with amino groups.[13] The crude product was treated with acetic anhydride to give an acetylated β-CyD bonded with seven TEMPO adducts, **1**, in 63% yield. The initiator **1** is soluble in common organic solvents.

Table 1. Characterizations of 2[a]

sample	$M_{w,SEC} \times 10^{-4}$ [b]	M_w/M_w [b]	$M_{w,SLS} \times 10^{-4}$ [c]	$[\eta]$,[d] dL·g^{-1}	$([\eta]_{lin}$[e])	$[\alpha]_D$,[f] deg	N_{PSt}[g]
2-I	1.34	1.03	2.98	0.091	(0.203)	+6.8	10.6
2-II	4.52	1.05	6.77	0.236	(0.380)	+2.1	7.0
2-III	13.5	1.06	18.7	0.620	(0.797)	+1.4	6.9
2-IV	96.7	1.06	189	2.085	(4.330)	+0.6	7.2

[a] Prepared through the fractionation of **I**−**IV** using preparative SEC. [b] Determined by SEC in $CHCl_3$ using linear polystyrene standards. [c] Determined by SLS measurements in toluene at 25 °C. [d] Determined by viscometry in benzene at 25 °C. [e] Calculated from the equation cited in ref 15. [f] Measured in $CHCl_3$ at 20 °C (*c* 1.0). [g] The arm-number calculated from eq 1.

Scheme 2. Synthesis of 1[a]



[a] Key: (i) Coupling reaction using DCC in DMF in the presence of HBT and Et_3N; (ii) acetylation using Ac_2O in pyridine.

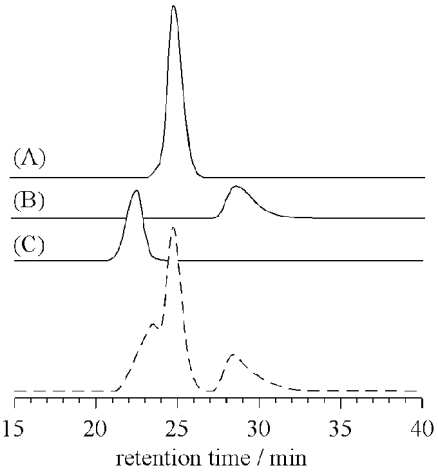


Figure 3. SEC traces of (A) **2-III**, (B) **3-III**, and (C) **4-III**, which were prepared through fractionations of **III** (shown as broken line).

Synthesis and Characterization of a Seven-Arm PSt with an Acetylated β-CyD Core, 2. Initially, we performed bulk polymerization of styrene (St). Size exclusion chromatography (SEC) traces of the products exhibited three peaks, i.e., the main peak along with the undesirable shoulders or peaks in both the higher and lower molecular weight regions. Thus, the uncontrolled byproducts were formed in the polymerization system. It should be noted that the relative amounts of the undesirable products increased with the increasing polymer yield.

The use of an appropriate solvent is one method to suppress the polymer yield.[14] Hence, chlorobenzene was used in the polymerization system. St was polymerized with **1** in chlorobenzene (St/chlorobenzene = 1/2, w/w) at 125 °C. The polymerization using an [St]/**1** of 7.5×10^3 for 2.5 h afforded a product, i.e., original product **II**, in 11% yield, which was based on the consumption of St. Figure 1B shows the SEC chromatogram of **II** with an $M_{w,SEC}$ of 4.32×10^4 and an M_w/M_n of 1.14. Although the uncontrolled products appeared in both the higher and lower molecular weight regions, their amounts might be significantly smaller due to the low yield.

The same polymerization was performed for the longer polymerization time of 10 h. The polymerization afforded a product, i.e., the original product **III** in 37% yield. Figure 1C shows the SEC chromatogram of **III**, which exhibited three peaks with an $M_{w,SEC}$ of 1.77×10^5 and an M_w/M_n of 2.93. As expected, the relative amounts of the undesirable product were significantly larger for **III** than that for **II**. Therefore, a way of suppressing the formation of the byproduct might be lowering the polymer yield. The origin of the byproduct is discussed in the following sections.

We focused our attention on characterizations of the main product in the original products. Hence, the original product was fractionated using preparative SEC to give the main product **2**. Table 1 summarizes the characterizations of **2**. Figure 2A shows, for example, the SEC chromatogram of **2-II**, which exhibited one peak with an $M_{w,SEC}$ of 4.52×10^4 and a low M_w/M_n of 1.05. The $M_{w,SEC}$ value was the apparent molecular weight on the basis of linear polystyrene (PSt) standards. Thus, an absolute weight-average molecular weight of **2** was determined by SLS measurements ($M_{w,SLS}$). The $M_{w,SLS}$ of 6.77×10^4 for **2-II** was greater than the $M_{w,SEC}$ values, indicating that the hydrodynamic volume of **2-II** was considerably smaller compared to the linear PSt with the same molecular weight.

In general, a star polymer shows a characteristic intrinsic property, i.e., a low viscosity. The intrinsic viscosity for **2**, $[\eta]$, is expected to be lower than that for a linear polystyrene with the same molecular weight, $[\eta]_{lin}$, which can be calculated from the literature.[15] The $[\eta]$ of 0.236 for **2-II** was apparently a lower value than the $[\eta]_{lin}$ of 0.380.

Similarly, the main product of the original product **III** was fractioned by preparative SEC affording a main product **2-III** with an $M_{w,SEC}$ of 1.35×10^5 and an M_w/M_n of 1.06 (Figure 3A). The $M_{w,SLS}$ of 1.87×10^5 was larger than the $M_{w,SEC}$ values. In addition, the $[\eta]$ of 0.620 for **2-III** was lower than the $[\eta]_{lin}$ of 0.797. Consequently, the $M_{w,SEC}$, $M_{w,SLS}$ and $[\eta]$ values indicated that **2** was assignable to a star polymer.

To facilitate the detection of NMR resonances for the star polymer **2**, St was polymerized with **1** using a low [St]/[**1**] value. The polymerization was performed using an [St]/[**1**] of 6.9×10^2 in chlorobenzene (St/chlorobenzene = 1/2, w/w) for 10 h at 125 °C to afford an original product **I** in a 37% yield. Figure 1A shows the SEC chromatogram of **I** with an $M_{w,SEC}$ of 1.42×10^4 and an M_w/M_n of 1.19. The amounts of the uncontrolled products for **I** were apparently smaller than those for **III**, although the polymerization time was constant at 10 h. Thus, a high [St]/[**1**] value was likely to produce the uncontrolled products. The fractionation of **I** using

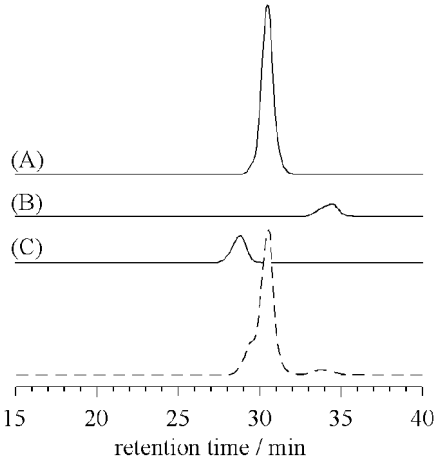


Figure 4. SEC traces of (A) **2-I**, (B) **3-I**, and (C) **4-I**, which were prepared through fractionations of **I** (shown as broken line).

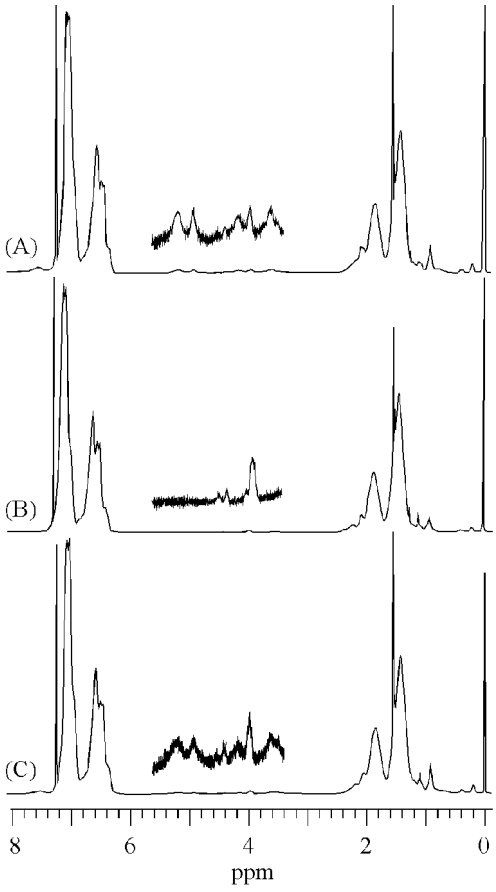


Figure 5. ^{1}H NMR spectra of (A) **2-I**, (B) **3-I**, and (C) **4-I** in $CDCl_3$.

preparative SEC afforded a star polymer **2-I**. Figure 4A shows the SEC trace of **2-I**, which exhibits one peak with an $M_{w,SEC}$ of 1.34×10^4 and an M_w/M_n of 1.03.

Figure 5A shows the ^{1}H NMR spectrum of **2-I**. The signals due to PSt appeared at 1.0−2.5 ppm and 6.2−7.4 ppm along with the characteristic signal due to the **1** unit at 0.1−1.0 ppm (the methyl protons in the TEMPO moiety) and 3.4−5.4 ppm (the methine protons in the acetylated β-CyD moiety). Hence, **2** was assignable to the product initiated by **1**, i.e., star PSt with an acetylated β-CyD core.

Bulk polymerization of St with **1** was carried out under a somewhat uncommon condition of a higher [St]/[**1**] value of 1.8×10^5 at 125 °C. The polymerization performed for 1 h to give original product **IV** with the 11% yield. Figure 1D shows the SEC trace of **IV**, which exhibits three peaks with an $M_{w,SEC}$ of 1.04×10^6 and an M_w/M_n of 4.26. The relative amounts of undesirable products were significantly large; however, the polymerization provided a product with a higher molecular weight. The fractionation of **IV** using preparative SEC successfully afforded a star polymer **2-IV** with a higher $M_{w,SLS}$ value of 1.89×10^4 and an M_w/M_n value of 1.17 (Figure 6A).

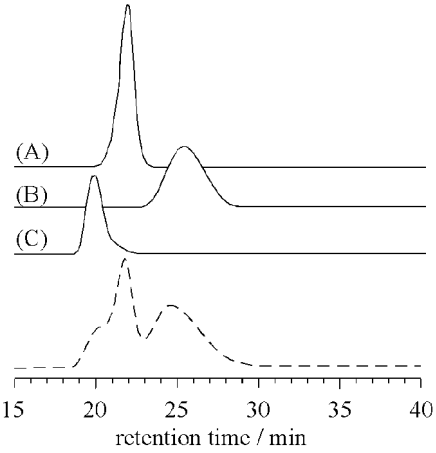


Figure 6. SEC traces of (A) **2-IV**, (B) **3-IV**, and (C) **4-IV**, which were prepared through fractionations of **IV** (shown as broken line).

Table 2. Characterizations of 2′ [a] and 4′ [b]

sample	$M_{w,SEC} \times 10^{-4}$ [c]	M_w/M_w [c]	sample	$M_{w,SEC} \times 10^{-4}$ [c]	M_w/M_w [c]
2′-I	0.280	1.24	**4′-I**		
2′-II	0.960	1.21	**4′-II**	0.985	1.20
2′-III	2.70	1.18	**4′-III**	2.82	1.18
2′-IV	26.1	1.30	**4′-IV**	25.8	1.35

[a] Prepared through the acid hydrolysis of **2**. [b] Prepared through the acid hydrolysis of **4**. [c] Determined by SEC in $CHCl_3$ using linear polystyrene standards.

To determine the arm number, N_{PSt}, **2** was treated with sulfuric acid, giving a core-cleaved polymer **2′**. The $M_{w,SEC}$ of **2′** was determined by SEC as listed in Table 2. Figure 7A shows the SEC chromatogram of **2′-III**, for example, which exhibited one narrow peak with an $M_{w,SEC}$ of 2.70×10^4 and an M_w/M_n of 1.18. The N_{PSt} of **2** should be defined by the following relation:

$$N_{PSt} = (M_{w,SLS} \text{ of } \mathbf{2})/(M_{w,SEC} \text{ of } \mathbf{2}') \qquad (1)$$

Equation 1 yielded the N_{PSt}'s of **2**, i.e., 10.6 for **2-I**, 7.0 for **2-II**, 6.9 for **2-III**, and 7.2 for **2-IV**, as listed in Table 1. Only the N_{PSt} of **2-I** was found to be significantly larger than seven. We would like to discuss this result on the basis of the fact that the molecular weight of **2′-I** ($M_{w,SEC} = 2800$) is the smallest in the four samples. In general, the terminal structure is likely to affect the SEC analysis, when the molecular weight of the polymer is low. There may be one possibility that the retention time of **2′-I** is delayed due to polar groups in the chain-end, giving an incorrect $M_{w,SEC}$ value, though it is known that the SEC analysis was not affected by hydrophilic interaction. However, the N_{PSt} values of **2-II**−**IV** ranged from 6.9 to 7.2. Therefore, **2** was assigned to a seven-arm star PSt with an acetylated β-CyD core.

Origin of Byproducts. Byproduct **3** was obtained as the species with lower molecular weight after frac-

Table 3. Characterization of Byproducts 3[a] and 4[a]

sample	$M_{w,SEC} \times 10^{-4}$ [c]	M_w/M_w[c]	$M_{w,SLS} \times 10^{-4}$ [c]	sample	$M_{w,SEC} \times 10^{-4}$ [c]	M_w/M_w[c]	$M_{w,SLS} \times 10^{-4}$ [c]
3-I	0.280	1.10		**4′-I**	2.71	1.03	
3-II	0.69	1.17		**4′-II**	10.5	1.05	17.2
3-III	2.30	1.22	2.50	**4′-III**	57.2	1.10	120
3-IV	11.0	1.35	12.0	**4′-IV**	391	1.27	883

[a] Prepared through the fractionation of **I**−**IV** using preparative SEC. [b] Determined by SEC in $CHCl_3$ using linear polystyrene standards. [c] Determined by SLS measurements in toluene at 25 °C. [d] Determined by viscometry in benzene at 25 °C.

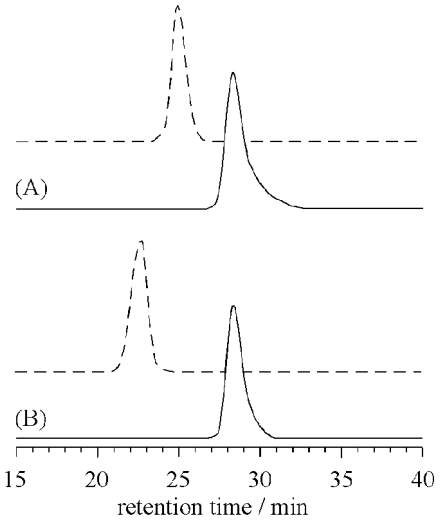
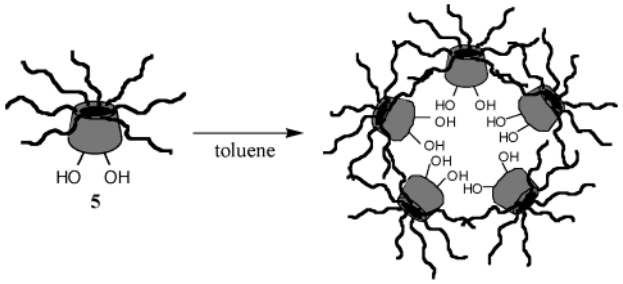


Figure 7. SEC traces of (A) **2′-III** and (B) **4′-III**, which were prepared through acid hydrolysis of **2-III** and **4-III** (shown as broken lines), respectively.

tionation of the original product using preparative SEC as before. Table 3 summarizes the characterizations of **3**. Figures 2B, 3B, 4B and 6B show the SEC traces of **3-II**, **3-III**, **3-I**, and **3-IV**, respectively. For example, the SEC chromatogram of **3-III** exhibited one peak with an $M_{w,SEC}$ of 2.30×10^4 and an M_w/M_n of 1.22. The $M_{w,SLS}$ of 2.50×10^4 for **3-III** was nearly consistent with the $M_{w,SEC}$ values, suggesting that **3-III** was assigned to linear PSt. Figure 5B shows the ^{1}H NMR spectrum of **3-I**. The signal due to PSt at 6.4−7.4 ppm and 1.0−2.4 ppm appeared along with the characteristic one due to the methyl protons of the TEMPO moiety at 0.5−1.0 ppm. In the expanded ^{1}H NMR spectrum in 3.5−4.6 ppm, the signal assignable to the methine proton near the chain end (−C*H*−ON−) appeared. However, the signals due to the acetylated β-CyD moiety did not appear. These results suggested that **3** was assignable to a TEMPO-terminated linear PSt, i.e., which was not initiated by **1**. A possible explanation for the formation of **3** might be as follows. For the TEMPO-mediated radical polymerization, the overall concentration of radical chain ends substantially decreased due to the presence of significant amounts of inactive chain ends, leading to a lower occurrence of undesirable side reactions such as termination, disproportionation, or a combination of these. This enables the polymer chain to grow in a controlled, or pseudo-living, process.[5e,h] However, the concentration of the inactive chain ends might be locally very low for the polymerization system with the multifunctional TEMPO initiator **1**, giving an uncontrolled product such as **3**. This explanation should be supported by the fact that a high [St]/[**1**] value was likely to produce the uncontrolled products.

Byproduct **4** was obtained as the species with higher molecular weight after fractionation of the original product using preparative SEC as before. Table 3 summarizes the characterizations of **4**. Figures 2C, 3C, 4C, and 6C show the SEC traces of **4-II**, **4-III**, **4-I**, and **4-IV**, respectively. For example, the SEC traces of **4-III** exhibited one narrow peak with an $M_{w,SEC}$ of 5.72×10^5 and an M_w/M_n of 1.10. The $M_{w,SLS}$ of **4-III** was found to be 1.40×10^6. The fact that the $M_{w,SLS}$ was considerably larger than the $M_{w,SEC}$ suggested that **4** might be assignable to a star polymer. Figure 5C shows the ^{1}H NMR spectrum of **4-I**. In the expanded ^{1}H NMR spectrum in 3.4−5.6 ppm, the signal assignable to the acetylated β-CyD moiety appeared. Therefore, **4** might be the product initiated by **1**. The byproduct **4** was treated with sulfuric acid, giving a core-cleaved polymer **4′**. Figure 7B shows the SEC trace of **4′-III** with an $M_{w,SEC}$ of 2.82×10^4 and an M_w/M_n of 1.18. Interestingly, the $M_{w,SEC}$ of the **4′-III** was quite similar value to that for **2′-III**. Therefore, **4** might be assigned to a kind of star−star coupled polymer, which was produced through the combination of **2**.

Scheme 3. Self-Assembled Aggregates of 5 in a Good Solvent for PSt[a]



[a] There are 14 hydroxyl groups at the C-2 and C-3 positions of the β-CyD. This illustration omits many of them.

Aggregation Property of a Seven-Arm PSt with a β-CyD. Polymer **2** was modified into a seven-arm PSt with a β-CyD, polymer **5**, using sodium methoxide in dry THF. Scheme 3 illustrates a characteristic structure of **5**; i.e., a total of 14 hydroxyl groups at the C-2 and C-3 positions of the β-CyD are located on the opposite side to the seven PSt arms at the C-6 positions. Hence, **5** is expected to self-assemble by intermolecular aggregations of the hydroxyl groups in a good solvent for PSt. To estimate such an aggregation property, the SLS measurements were performed in toluene. The $M_{w,SLS}$ values were found to be 3.96×10^5 for **5-I**, 3.78×10^5 for **5-II**, 2.40×10^5 for **5-III**, and 1.94×10^6 for **5-IV** (Table 4). The average aggregation numbers (N_A) of **5** should be defined by the following relation:

$$N_A = (M_{w,SLS} \text{ of } \mathbf{5})/(M_{w,SLS} \text{ of } \mathbf{2}) \qquad (2)$$

Equation 2 yielded the N_A of **5**, i.e., 13 for **5-I**, 6 for **5-II**, 1.3 for **5-III**, and 1.0 for **5-IV**, as listed in Table 4. These results indicated that the β-CyD in the cores of **5-I** and **5-II** acted as a hydrophilic unit to form unique self-assembled aggregates in a good solvent for PSt as illustrated in Scheme 3.

Table 4. Aggregation Property of 5[a]

sample	$M_{w,SLS} \times 10^{-4}$ [c]	N_A[c]
5-I	39.6	13
5-II	37.8	5.6
5-III	24.0	1.3
5-IV	194	1.0

[a] Prepared through the deacetylation of **2**. [b] Determined by SLS measurements in toluene at 25 °C. [c] Aggregation number calculated from eq 2.

Conclusions

β-CyD was modified into the seven-functional initiator (**1**) for TEMPO-mediated living radical polymerization. The main product obtained through the polymerization of St with **1** was assigned to a seven-arm star PSt with an acetylated β-CyD core, **2**. The byproducts formed in the St/**1** system were found to be a TEMPO-terminated linear PSt, **3**, and a star−star coupled polymer, **4**. The seven-arm star PSt with a β-CyD core, **5**, which was obtained through deacetylation of **2**, showed a self-assembling property in a good solvent for PSt. Thus, initiator **1** was one of the useful tools for constructing a star polymer with a definite arm number and also a functional core.

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