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Original Article

Synthesis of a star-shaped poly(ε-caprolactone) with a cyclodextrin core

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ABSTRACT

The preparation of star polymers bearing seven linear poly(ε-caprolactone) arms linked to a β-cyclodextrin (β-CD) core is described. The hydroxyl groups at C6 of β-CD were selectively protected with a *tert*-butyldimethylsilyl (TBDMS) group, and then the remaining hydroxyl groups at C2 and C3 were subsituted with a benzyloxy group. The TBDMS groups were removed to give a cyclodextrin derivative **3** with seven free primary hydroxyl groups. The controlled ring-opening polymerization of ε-caprolactone (ε-CL) was carried out using the multifunctional initiator **3** with stannous octoate ($Sn(Oct)_2$) as the catalyst to obtain a star-shaped poly(ε-CL) (**4**). After the polymerization proceeded sufficiently, the addition of another portion of ε-CL to the system afforded **4** with longer arm length. Debenzylation of **4** was successfully achieved by catalytic hydrogenolysis on $Pd(OH)_2/C$ to produce a star-shaped poly(ε-CL) with a hydrophilic moiety of β-CD as the core.

KEYWORDS: star polymer, cyclodextrin, controlled polymerization, polyester.

INTRODUCTION

Star-shaped polymers are a unique class among branched polymers, and are defined as macromolecules in which several linear polymers called “arms” are radially linked to a center called “core” [1]. In the synthesis of star polymers, polymerization is usually carried out in a controlled/living manner because uniform arm length is required for the homogeneous shape and size of the resulting product. It is known that ε-caprolactone (ε-CL), a cyclic ester, is ring-opening polymerized in a living manner under suitable conditions [2-4] to give a polymer with a uniform molecular weight. Poly(ε-CL) is highly crystalline but biodegradable, and hence has been drawing attention as a ‘green’ polymer. The mechanical strength and Young’s modulus of poly(ε-CL) are not very high compared to those of other engineering plastics, therefore, poly(ε-CL) has been used in low mechanical load-bearing applications such as the production of medical materials, packaging materials, drug delivery systems, etc. An example study illustrating the utilization of the properties of poly(ε-CL) [5] reported that microcapsules made of poly(ε-CL) containing lactic acid bacteria inside them, can gradually biodegrade which control-releases the lactic acid bacteria responsible for soil bioamendment. On the other hand, since poly(ε-CL) is hydrophobic, it is necessary to form a complex that imparts hydrophilicity for use *in vivo*. Amphiphilic block copolymers consisting of poly(ε-CL) and monomethylated polyethylene glycol having a number-average molecular weight of 2,000 or 5,000 have been synthesized by controlled ring-opening polymerization of ε-CL [6], and are considered for use in drug delivery and tissue engineering. Zinck *et al.* synthesized biocompatible materials through the polymerization of ε-CL from water soluble polysaccharides such as dextran and partially methylated cellulose in water [7].

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Cyclodextrins (CDs) are cyclic oligosaccharides in which six, seven, or eight D-glucoses are linked together by 1,4-α glycosidic bonds and named α-, β-, and γ-CD, respectively. They have interesting shapes, such as truncated conical, resulting in good rotational symmetry. One of the unique properties of CDs is that they can form inclusion complexes. On the narrower opening, the primary hydroxyl groups at the C6 positions are present toward the outside, whereas on the wider opening, the secondary hydroxyl groups at the C2 and C3 positions exist in the outward direction. As the result, the inside of CDs becomes hydrophobic due to the absence of hydroxyl groups, and hydrophobic molecules that fit the size of the cavity enter inside [8]. Several studies on the synthesis of star polymers with a CD core have been reported [9-11]. However, they were synthesized by linking an initiator to a CD, followed by atom transfer radical polymerization [9, 10] or 2,2,6,6-tetramethylpiperidinyloxy-mediated living radical polymerization [11] of vinyl monomers from the initiator attached to the CD.

In the present study, we attempt the controlled ring-opening polymerization of ε-CL directly from the hydroxyl groups of the CD which is the core and initiator. In particular, the primary hydroxyl groups at the C6 of the CD are highly reactive and have less steric hindrance compared to the C2 and C3 hydroxyl groups. If the polymerization can be initiated only from the C6 hydroxyl groups, the C2 and C3 hydroxyl groups in the wider opening of the CD core are still free and the ability to form inclusion complexes will still remain. As another application, the remaining C2 and C3 hydroxyl groups can be reacted with other functional molecules such as hydrophilic polymers. Here, we describe the synthesis of star-shaped polymers having seven linear poly(ε-CL) arms linked directly to the C6 hydroxyl groups on the β-CD core.

MATERIALS AND METHODS

General

All chemicals were used as received without further purification unless stated. β-CD (Wako Pure Chemical Industries, Japan) was dried in a vacuum oven at 100 °C for 12 h before use. Sodium hydride (Kishida Chemical, Japan) was used after being washed with hexane to remove the coating of mineral oil. Tetrahydrofuran (THF) used for polymerization was obtained from Sigma-Aldrich, Japan, in the anhydrous and inhibitor-free form, and distilled in the presence of CaH_2 just before use. IR spectrum was measured on a JASCO FT/IR-4600 spectrometer using a KBr pellet. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECX400 spectrometer at 400 MHz and 100 MHz, respectively, in $CDCl_3$ at 27 °C. The chemical shift was referenced to 7.26 ppm and 77.0 ppm for ^{1}H and ^{13}C), respectively, of the solvent signal. Double-quantum filtered correlation spectroscopy (DQF-COSY), heteronuclear single quantum coherence (HSQC), and hetereonuclear multiple-bond connectivity (HMBC) measurements were performed using field gradient pulses. The evolution delay for the HMBC experiments was set to 60 ms. Elemental analyses were performed on a J-Science Lab Micro Corder JM10. Preparative high-performance liquid chromatography (HPLC) was conducted using a Wako Pure Chemical Industries Wakosil 5SIL silica gel column. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of polymers were estimated by means of gel permeation chromatography (GPC) calibrated with standard polystyrenes (Showa Denko, Shodex SM-105) in $CHCl_3$. Three Tosoh TSKgel columns of G2500H_{XL}, G3000H_{XL}, and G4000H_{XL} were connected in series. The M_n of the polymers was also calculated using the ^{1}H NMR spectrum.

Synthesis of heptakis(6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin (1)

Commercial β-CD (5.67 g, 5.00 mmol) was treated with *tert*-butyldimethylsilyl chloride in pyridine, according to the literature [12] with slight modifications. The crude product obtained was chromatographed on silica gel (chloroform/methanol 3/1 as eluent) to give 6.97 g (72.1%) of **1** as white crystals. Anal. Calcd for $C_{84}H_{168}O_{35}Si_7$ (1934.8): C, 52.15; H, 8.75. Found: C, 52.24; H, 8.72. IR (KBr, cm^{-1}): 3363 (br, OH), 1255 and 837 (m, Si–C). ^{1}H NMR ($CDCl_3$, ppm): δ 0.03 (s, 21H, Si–CH_3), 0.04 (s, 21H, Si–CH_3), 0.89 (s, 63H, C(CH_3)$_3$), 3.56 (dd, 7H, H4, $J_{3,4}$ = 8.97 Hz, $J_{4,5}$ = 9.34 Hz), 3.62–3.66 (m, 14H, H2 and H5), 3.71 (d, 7H, H6,

$J_{6,6'}$ = 9.34 Hz), 3.90 (dd, 7H, H6', $J_{5,6'}$ = 2.93 Hz, $J_{6,6'}$ = 9.34 Hz), 4.04 (dd, 7H, H3, $J_{2,3}$ = 9.15 Hz, $J_{3,4}$ = 8.97 Hz), 4.89 (d, 7H, H1, $J_{1,2}$ = 3.48 Hz), 5.26 (s, 7H, C2–OH), 6.73 (s, 7H, C3–OH). ^{13}C NMR ($CDCl_3$, ppm): δ –5.2 (Si–CH_3), –5.1 (Si–CH_3), 18.3 ($C(CH_3)_3$), 25.9 (C(CH_3)$_3$), 61.6 (C6), 72.6 (C5), 73.4 (C3), 73.6 (C2), 81.8 (C4), 102.0 (C1).

Synthesis of heptakis(2,3-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin (2)

To a solution of **1** (5.80 g, 3.00 mmol) in *N*,*N*-dimethylformamide (100 mL) benzyl bromide (3.0 mL, 25 mmol) and NaH (0.6 g, 25 mmol) were added with stirring at 0 °C under N_2 atmosphere. After 12 h of stirring at room temperature, an excess amount of methanol was added dropwise to the solution. The mixture was concentrated *in vacuo* and the residue was diluted with chloroform and water. The separated chloroform layer was washed with water two times, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by silica gel chromatography (chloroform/ethyl acetate 10/1 as eluent) repeatedly, affording 7.95 g (83.0%) of **2** as colorless syrup. Anal. Calcd for $C_{182}H_{252}O_{35}Si_7$ (3196.6): C, 68.39; H, 7.95. Found: C, 68.50; H, 7.90. IR (KBr, cm^{-1}): 3089, 3064, 3032, 1604, 733, and 697 (w, aromatic), 1254 and 834 (m, Si–C). ^{1}H NMR ($CDCl_3$, ppm): δ 0.06 (s, 21H, Si–CH_3), 0.07 (s, 21H, Si–CH_3), 0.92 (s, 63H, C(CH_3)$_3$), 3.44 (dd, 7H, H2, $J_{1,2}$ = 3.30 Hz, $J_{2,3}$ = 9.34 Hz), 3.76 (dd, 7H, H6, $J_{5,6}$ = 1.28 Hz, $J_{6,6'}$ = 9.70 Hz), 3.74–3.80 (m, 7H, H5), 4.05 (dd, 7H, H4, $J_{3,4}$ = 8.70 Hz, $J_{4,5}$ = 8.97 Hz), 4.11 (dd, 7H, H3, $J_{2,3}$ = 9.34 Hz, $J_{3,4}$ = 8.70 Hz), 4.31 (d, 7H, H6', $J_{6,6'}$ = 9.70 Hz), 4.56 (dd, 14H, O2–CH_2Ph, J = 12.08, 17.21 Hz), 4.94 (dd, 14H, O3–CH_2Ph, J = 10.98, 146.0 Hz), 5.36 (d, 7H, H1, $J_{1,2}$ = 3.30 Hz), 7.09–7.21 (m, 70H, phenyl×14). ^{13}C NMR ($CDCl_3$, ppm): δ –5.1 (Si–CH_3), –4.8 (Si–CH_3), 18.3 ($C(CH_3)_3$), 26.0 (C(CH_3)$_3$), 62.4 (C6), 72.6 (C5, O2–CH_2Ph), 75.5 (O3–CH_2Ph), 77.7(C4), 79.3 (C2), 80.9 (C3), 97.9 (C1), 126.8–139.3 (phenyl).

Synthesis of heptakis(2,3-di-*O*-benzyl)-β-cyclodextrin (3)

A solution of tetrabutylammonium fluoride in THF (1.0 mol/L, 10 mL) was added to a solution of **2** (3.20 g, 1.00 mmol) in THF (50 mL) with stirring at room temperature. The mixture was refluxed at 70 °C for 2 h under N_2 atmosphere, and then concentrated at 40 °C *in vacuo*. A solution of the residue in chloroform was washed with water twice, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Silica gel chromatography (chloroform/methanol 8/1 as eluent) of the residue gave 2.83 g (92.0%) of **3** as colorless syrup. Anal. Calcd for $C_{140}H_{154}O_{35}$ (2396.7): C, 70.15; H, 6.48. Found: C, 70.13; H, 6.49. IR (KBr, cm^{-1}): 3465 (br, OH), 3087, 3063, 3030, 1604, 1496, 1453, 736, and 698 (m, aromatic). ^{1}H NMR ($CDCl_3$, ppm): δ 3.47 (dd, 7H, H2, $J_{1,2}$ = 3.66 Hz, $J_{2,3}$ = 8.79 Hz), 3.63 (t, 7H, H4, $J_{3,4}$ = $J_{4,5}$ = 8.42 Hz), 3.78 (dd, 7H, H6, $J_{5,6}$ = 4.39 Hz, $J_{6,6'}$ = 11.7 Hz), 3.85–3.98 (m, 21H, H3, H5, H6'), 4.48 (dd, 14H, O2–CH_2Ph, J = 12.26, 33.68 Hz), 4.77 (dd, 14H, O3–CH_2Ph, J = 11.17, 75.05 Hz), 4.80 (br, 7H, OH), 5.01 (d, 7H, H1, $J_{1,2}$ = 3.66 Hz), 6.96–7.34 (m, phenyl×14). ^{13}C NMR ($CDCl_3$, ppm): δ 61.6 (C6), 72.8 (O2–CH_2Ph), 73.0 (C5), 74.9 (O3–CH_2Ph), 78.4 (C2), 78.7 (C4), 80.4 (C3), 98.3 (C1), 127.1–139.0 (phenyl).

Ring-opening polymerization of ε-CL initiated from 3

The ring-opening polymerization of ε-CL was carried out under high vacuum conditions (~10^{-6} Torr) as reported previously [13]. THF (4 mL) was distilled into an ampoule containing **3** (72.0 mg, 3.00×10^{-2} mmol) and ε-CL (480 mg, 4.20 mmol). A solution of $Sn(Oct)_2$ (8.5 mg, 2.1×10^{-2} mmol) in THF (1 mL) was added to the ampoule, and then the mixture was stirred at 70 °C for 24 h. After the polymerization was quenched by adding a small amount of 5% HCl aqueous solution at room temperature, the mixture was diluted with chloroform and neutralized with aqueous $NaHCO_3$. The separated chloroform layer was washed with water three times, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by reprecipitation with THF–methanol three times and freeze-dried from benzene to give 530 mg (96.0%) of white solid **4**. Whether polymeric products still remained in the supernatant after reprecipitation or not was confirmed by GPC.

During the same polymerization as above, another portion of ε-CL (240 mg, 2.10 mmol) was added after 24 h from the start of the polymerization. After a further 12 h of stirring, the reaction mixture was

terminated and treated using the same procedure as above, resulting in 737 mg (93.1%) of **4**. IR (KBr, cm^{-1}): 3438 (br, OH), 3085, 3063, 3031, 1603, 1497, 1459, 733, and 699 (m, aromatic), 1725 (s, C=O). ^{1}H NMR ($CDCl_3$, ppm): δ 1.35–1.42 (m, H_γ), 1.61–1.69 (m, H_β, H_δ), 2.31 (t, H_α, J = 7.50 Hz), 2.37 (t, initial H_α, J = 7.50 Hz), 3.65 (t, terminal H_ε, J = 6.59 Hz), 4.06 (t, H_ε, J = 6.77 Hz), 3.48–5.12 (H1–H6, –C*H*$_2$Ph), 7.18 (br, phenyl). ^{13}C NMR ($CDCl_3$, ppm): δ 24.6 (C_γ), 25.5 (C_β), 28.3 (C_δ), 34.1 (C_α), 62.7 (terminal C_ε), 64.1 (C_ε), 63–80 (br, C2–C6, Ph*C*H$_2$–), 98.7 (C1), 127.1–128.2 and 138.1–139.2 (Phenyl), 173.5 (C=O).

Debenzylation of polymer 4

To a solution of **4** (184 mg) in THF (5 mL) and acetic acid (1 mL) ($Pd(OH)_2$ on carbon (180 mg) was added. The mixture was stirred at room temperature for 3 days under 0.3 MPa of H_2, and then filtered using a glass filter. The filtrate was diluted with chloroform and water, and neutralized with aqueous $NaHCO_3$. The separated chloroform layer was washed with water three times, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by reprecipitation with THF−methanol three times and freeze-dried from benzene to produce 143 mg (83.5%) of white solid **5**. IR (KBr, cm^{-1}): 3360 (br, OH), 1725 (s, C=O). ^{1}H NMR ($CDCl_3$, ppm): δ 1.35–1.44 (m, H_γ), 1.60–1.69 (m, H_β, H_δ), 2.31 (t, H_α, J = 7.50 Hz), 2.31 (t, initial H_α, J = 7.51 Hz), 3.65 (t, terminal H_ε, J = 6.58 Hz), 4.06 (t, H_ε, J = 6.77 Hz), 3.55–6.65 (H1–H6, OH). ^{13}C NMR ($CDCl_3$, ppm): δ 24.5 (C_γ), 25.5 (C_β), 28.3 (C_δ), 34.1 (C_α), 62.7 (terminal C_ε), 64.1 (C_ε), 65–82 (br, C2–C6), 102.6 (C1), 173.5 (C=O).

RESULTS AND DISCUSSION

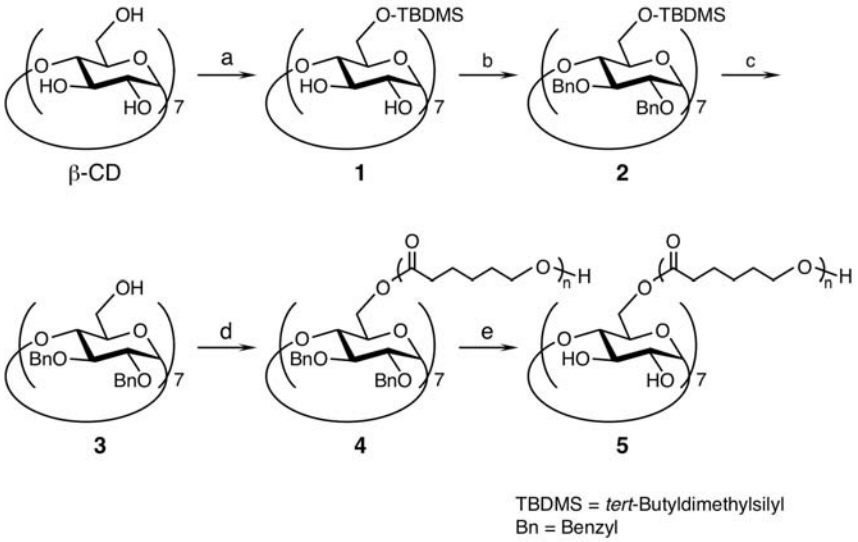
Synthesis of a CD-based multifunctional initiator

For the preparation of a seven-armed star polymer, a β-CD derivative with seven free hydroxyl groups on only the C6 positions was synthesized as the multifunctional initiator. First, as shown in Scheme 1, all the hydroxyl groups on the C6 of β-CD were selectively protected with a *tert*-butyldimethylsilyl (TBDMS) group, by the method of Fügedi [12], because of the difficulty of the selective protection of the C2 and C3 hydroxyl groups. The expected product, heptakis(6-*O*-TBDMS)-β-CD (**1**) was obtained in 72% yield, with minor oversilylated products. Conventional benzylation of the hydroxyl groups on the C2 and C3 of **1** and subsequent deprotection of the TBDMS groups on the C6 by using tetrabutylammonium fluoride (TBAF) were accomplished to afford heptakis(2,3-di-*O*-benzyl)-β-CD (**3**). The IR spectrum of **3** proved the existence of hydroxyl and benzyl groups at 3465 cm^{-1} and 1604 cm^{-1}, respectively. Figure 1(A) shows the ^{1}H NMR spectrum of **3** in $CDCl_3$. Each peak was assigned by DQF-COSY spectrum. There is only one peak for each positional proton derived from the seven pyranose rings, suggesting that all the seven pyranose rings are equivalent and that the chemical structure has seven-fold symmetry. Two methylene peaks of the benzyl group on C2 and C3 appear at 4.48 ppm and 4.77 ppm, respectively, and no signal from a TBDMS group can be seen. No impurities other than water were detected in the spectrum. The elemental analysis of **3** agreed with the calculated one. These analytical results are consistent with the structure of **3**.

Synthesis of a star-shaped poly(ε-CL) with a β-CD core

As shown in Scheme 1, the synthesis of a star-shaped poly(ε-CL) was conducted by ring-opening polymerization of ε-CL using initiator **3** and $Sn(Oct)_2$ as the catalyst. The reaction was executed under high vacuum in order to prevent moisture in the air, proceeded homogeneously without precipitations, and was terminated with dilute HCl. The resulting product was purified by reprecipitation from the chloroform solution with methanol, and lyophilized from the benzene solution. The supernatant after reprecipitation was analyzed by thin-layer chromatography and GPC; no detectable ε-CL and **3** were observed. The yield of the product was 96.0%, indicating that most of the ε-CL used was converted into the polymer.

Figure 1(B) shows the ^{1}H NMR spectrum of the product after being lyophilized. The four large peaks in the range of 1 to 4 ppm were found to be the H_α to H_ε protons of poly(ε-CL) [14]. In addition, small broad peaks appeared in the region from 3.2 to 5.4 ppm and at 7 ppm. They were assigned to the protons of the β-CD moiety and



Scheme 1. Synthesis of seven-armed star-shaped poly(ε-CL) with a β-CD core. Reagents and conditions: (a) TBDMS-Cl, Py, rt, 24 h; (b) BnBr, NaH, DMF, rt, 24 h; (c) TBAF, THF, 70 °C, 2 h; (d) ε-CL, $Sn(Oct)_2$, THF, 24 h, 70 °C; (e) H_2, $Pd(OH)_2/C$, AcOH, THF, rt, 3 d.

the terminal H_ε of poly(ε-CL) [14], and phenyl protons of the benzyl groups, respectively. Analysis revealed that the integration ratio of the phenyl protons to the terminal H_ε was 5.3, which is close to the theoretical value of 5.0 as in the case of when seven poly(ε-CL) chains are attached to the benzylated β-CD. The slight excess in this value is probably due to the overlap of the absorption of the phenyl groups and that of the residual $CHCl_3$. Therefore, it was concluded that the product is a graft polymer **4** having seven poly(ε-CL) chains attached onto heptakis(2,3-di-*O*-benzyl)-β-CD.

According to the Penczek and co-workers' report [15], the polymerization of ε-CL catalyzed by $Sn(Oct)_2$ is well-controlled, and takes place almost without termination and chain transfer. Hence, the present seven poly(ε-CL) chains linked to the benzylated β-CD core are considered to be of approximately equal length. The number-average degree of polymerization (DP_n) of each poly(ε-CL) arm was estimated to be 18 from the integration ratio of the terminal H_ε at 3.65 ppm to the H_α at 2.31 ppm in the ^{1}H NMR spectrum. This value is reasonably close to the theoretical value of DP_n = 20 calculated from the molar ratio of ε-CL to initiator **3** in feed. Figure 2(A) illustrates the GPC trace of this product. The molecular weight distribution (M_w/M_n) has a relatively narrow value of 1.19, suggesting that termination and/or chain transfer were hardly involved in this polymerization. The number-average molecular weight of 1.37×10^4 determined by GPC ($M_{n,GPC}$) was smaller than that calculated from the ^{1}H NMR spectrum ($M_{n,NMR}$) (1.60×10^4). This result also indicates that the resulting polymer is star-shaped; generally, star polymers have significantly different hydrodynamic radii compared to linear polymers due to their compact nature [1].

Further evidence of the living nature of the present polymerization was confirmed by a monomer addition experiment. During the polymerization under the same conditions as above, an additional portion of ε-CL (240 mg, 2.10 mmol) was introduced into the system after 24 h from the start of the polymerization. The mixture was subsequently stirred for 12 h, and the resulting product was analyzed by GPC. As shown in Figure 2(B), the curve B was unimodal and shifted to the higher molecular weight region compared to the curve A while maintaining a narrow distribution. This means that no homopolymer of the additional ε-CL was produced. The $M_{n,NMR}$, $M_{n,GPC}$, and M_w/M_n of the polymer obtained by the monomer addition experiment were 2.29×10^4, 1.99×10^4, and 1.14,

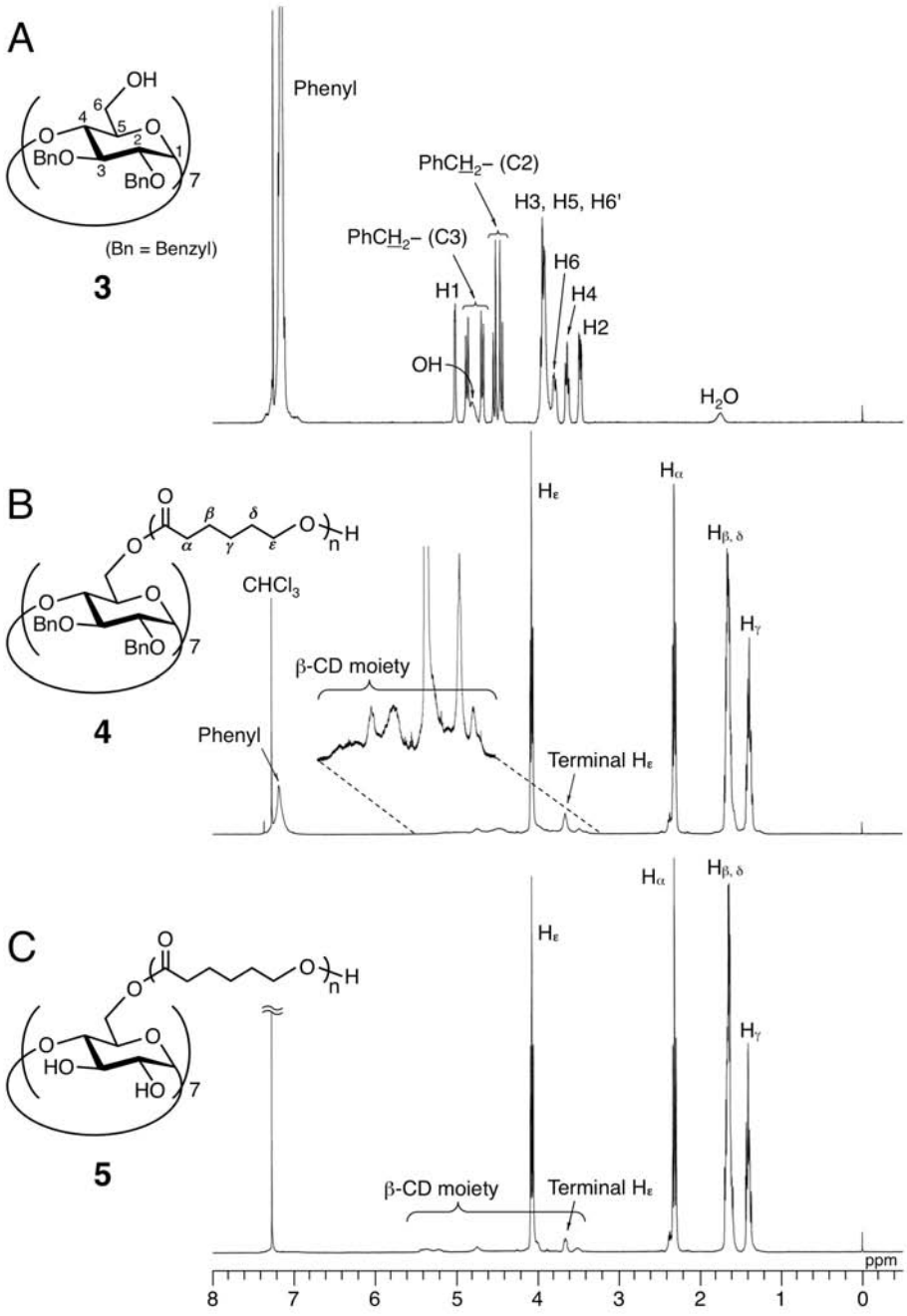


Figure 1. ^{1}H NMR spectra of **3** (A), **4** (B), and **5** (C) in $CDCl_3$.

respectively. It was found that the DP_n per each arm increased by 8.6, based on the ^{1}H NMR result. The theoretical elongation of DP_n per each arm is 10, close to the experimental value, thus the living nature was proved.

Debenzylation of **4** was conducted by catalytic hydrogenation using $Pd(OH)_2$ on carbon, for 3 days. The ^{1}H NMR spectrum of the product shown in Figure 1(C) indicates the absence of the phenyl protons of benzyl groups around 7 ppm. Furthermore, the IR spectrum of the product had a broad peak at 3358 cm^{-1} and no peak around 1600 cm^{-1}. Therefore, it was concluded that all the benzyl groups of **4** were removed completely. The resulting

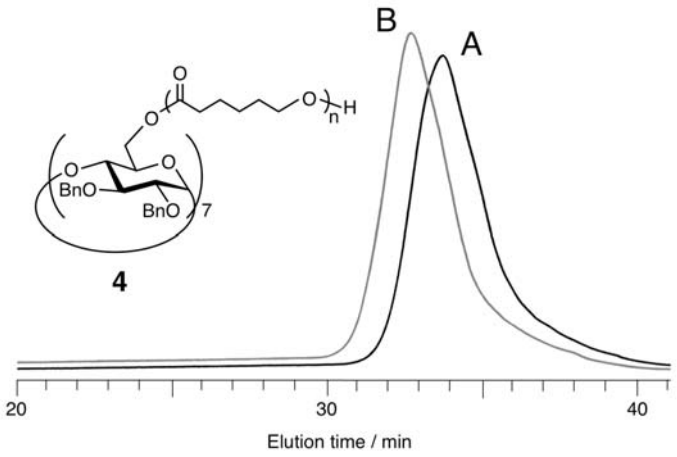


Figure 2. GPC curves of star-shaped poly(ε-CL) (**4**) with $M_{n,NMR}$ = 1.60 × 10^4 (A) and 2.29 × 10^4 (B). $M_{n,NMR}$ denotes the number-average molecular weight estimated from ^{1}H NMR spectrum.

star polymer still had 14 hydroxyl groups in the core where propagation of other arm polymers and/or chemical modification with other functional groups could be carried out, and hence, various applications for this polymer are expected.

CONCLUSIONS

In summary, this work demonstrated the synthesis of star-shaped polymers with seven arms of poly(ε-CL) linked to a β-CD core. This was accomplished by ring-opening polymerization of ε-CL from heptakis(2,3-di-*O*-benzyl)-β-CD which acts as a multifunctional initiator. The use of $Sn(Oct)_2$ as a catalyst allowed the polymerization to proceed in a living manner. The living nature was confirmed by a monomer addition experiment during polymerization. The DP_n of ε-CL unit calculated from the ^{1}H NMR spectrum increased from 17 to 26 in each poly(ε-CL) arm, sustaining a narrow molecular weight distribution. Hydrogenation of the resulting polymer with $Pd(OH)_2$/C gave star poly(ε-CL)s centered on a debenzylated β-CD.

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CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest.

REFERENCES

1. Ren, J. M., McKenzie, T. G., Fu, Q., Wong, E. H. H., Xu, J., An, Z., Shanmugam, S., Davis, T. P., Boyer, C. and Qiao, G. G. 2016, Chem. Rev., 116, 6743.
2. Slattery, R. M., Stahl, A. E., Brereton, K. R., Rheingold, A. L., Green, D. B. and Fritsch, J. M. 2019, J. Polym. Sci. Part A: Polym. Chem., 57, 48.
3. Makiguchi, K., Satoh, T. and Kakuchi, T. 2011, J. Polym. Sci. Part A: Polym. Chem., 49, 3769.
4. Naumann, S., Scholten, P. B. V., Wilson, J. A. and Dove, A. P. 2015, J. Am. Chem. Soc., 137, 14439.
5. Takei, T., Yoshida, M., Hatate, Y., Shiomori, K. and Kiyoyama, S. 2008, J. Biosci. Bioeng., 106, 268.
6. Hans, M., Gasteier, P., Keul, H. and Moeller, M. 2006, Macromolecules, 39, 3184.
7. Stanley, N., Bucataru, G., Miao, Y., Favrelle, A., Bria, M., Stoffelbach, F., Woisel, P. and Zinck, P. 2014, J. Polym. Sci. Part A: Polym. Chem., 52, 2139.
8. Szejtli, J. 1998, Chem. Rev., 98, 1743.
9. Xu, F. J., Zhang, Z. X., Ping, Y., Li, J., Kang, E. T. and Neoh, K. G. 2009, Biomacromolecules, 10, 285.
10. Lin, Y.-Y., Zhong, Y.-B., Nan, J.-K. and Tian, W. 2010, Macromolecules, 43, 10221.
11. Kakuchi, T., Narumi, A., Matsuda, T., Miura, Y., Sugimoto, N., Satoh, T. and Kaga, H. 2003, Macromolecules, 36, 3914.

12. Fügedi, P. 1989, Carbohydr. Res., 192, 366.
13. Hattori, K. and Yoshida, T. 2009, Macromolecules, 42, 6044.
14. Shi, X., Jing, Z., Zhang, G., Xu, Y. and Yao, Y. 2017, J. Appl. Polym. Sci., 134, 45575.
15. Kowalski, A., Duda, A. and Penczek, S. 1998, Macromol. Rapid Commun., 19, 567