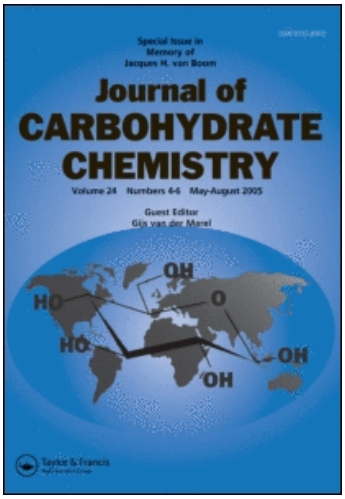

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Ken-Ichi Kanno[a]; Yuichi Kobayashi[a]; Shin-Ichiro Nishimura[b]; Hiroyoshi Kuzuhara[c]; Kenichi Hatanaka[a]
[a] Department of Biomolecular Engineering, Tokyo Institute of Technology, Yokohama, Japan [b] Division of Biological Science, Graduate School of Science, Hokkaido University, Sapporo, Hokkaido, Japan [c] Faculty of Engineering, Saitama University, Saitama, Japan

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Ken-Ichi Kanno,[a] Yuichi Kobayashi,[a] Shin-Ichiro Nishimura,[b]
Hiroyoshi Kuzuhara,[c] and Kenichi Hatanaka.[a*]

[a] Department of Biomolecular Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226, Japan.

[b] Division of Biological Science, Graduate School of Science, Hokkaido University, Sapporo 060, Hokkaido, Japan.

[c] Faculty of Engineering, Saitama University, 255 Shimo-ookubo, Urawa-shi 338, Saitama, Japan.

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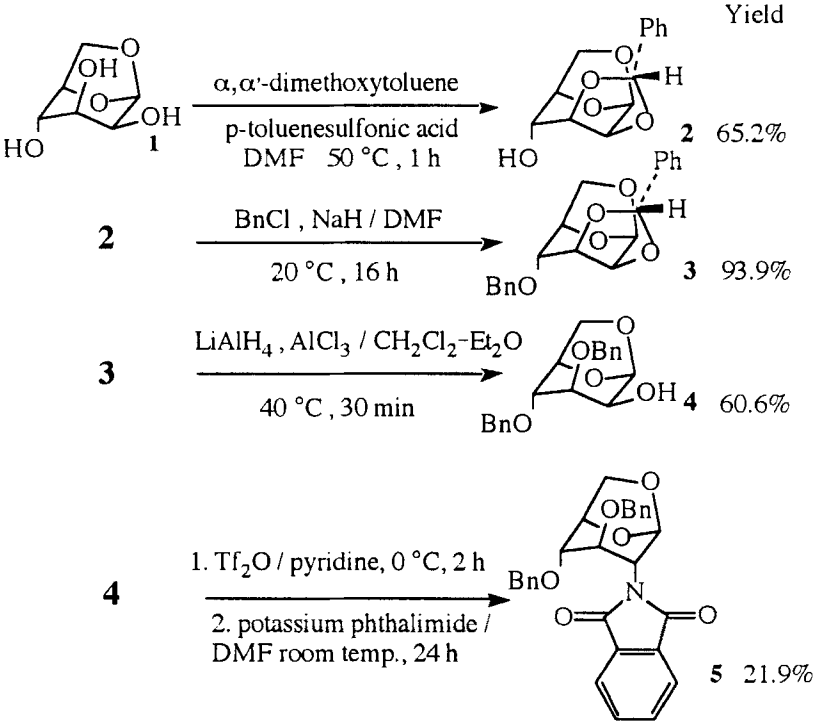
ABSTRACT

1,6-Anhydro-2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-β-D-glucopyranose (**5**) was synthesized from 1,6-anhydro-β-D-mannopyranose (**1**) in five steps. Compound **5** was polymerized under cationic conditions and selectively yielded glucosamine oligomers (degree of polymerization 5-7). Copolymerization of **5** with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose indicated the low reactivity of **5** with the active cation derived from **5**. Deprotection of 2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-(1→6)-β-D-glucopyranan (**7**) and *N*-acetylation gave 2-acetamido-2-deoxy-(1→6)-β-D-glucopyranan (**9**).

INTRODUCTION

Ring-opening polymerization of 1,6-anhydro sugars has been investigated using various anhydro hexose monomers and stereoregular glucopyranans containing amino groups have been synthesized.[2,3] However, the polymer of 2-amino-2-deoxy-D-glucopyranose, i.e. glucosamine, has not been synthesized by ring-opening polymerization. 2-Amino-2-deoxy-D-glucopyranose and 2-acetamido-2-deoxy-D-glucopyranose play important roles in living organisms, for instance, as core components of *N*-linked glycoproteins, glucosaminoglycans, and glycolipids. On the other hand, (1→4)-β-linked

N-acetyl-D-glucosamine (chitin), and its de-*N*-acetylated compound (chitosan) are natural biofunctional polysaccharides. Modifications and utilizations of both polysaccharides have been investigated.[4,5] (1→6)-β Linkages of 2-amino-2-deoxy-D-glucopyranose have been found in the branching core of numerous mammalian tissues.[6] In this study, 1,6-anhydro-2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-β-D-glucopyranose (**5**) was synthesized and polymerized under cationic conditions in order to give artificial (1→6)-linked D-glucosamine derivatives.



Scheme 1. Synthesis of 1,6-anhydro-2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-β-D-glucopyranose (**5**).

RESULTS AND DISCUSSION

Synthesis of 1,6-anhydro-2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-β-D-glucopyranose (5). 1,6-Anhydro-2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-β-D-glucopyranose (**5**) was synthesized from 1,6-anhydro-β-D-mannopyranose (**1**) in five steps (Scheme 1). As shown in Scheme 1, 1,6-anhydro-3,4-di-*O*-benzyl-β-D-mannopyranose (**4**) was first selectively synthesized from 1,6-anhydro-4-*O*-benzyl-2,3-*O*-(*S*)-benzylidene-β-D-mannopyranose (**3**) by reduction with lithium aluminum hydride

Table 1. Polymerization of **5**.[a]

No.	Initiator, mol%	Temp., °C	Time, h	Yield, %	$\overline{M}_n$ [b]	$\overline{DP}_n$	$[\alpha]_D^{22}$, deg.
1	1	0	48	9	3400	7	+52.2
2	10	0	48	48	3100	6.5	+63.0
3	10	-10	48	61	2800	6	+66.4
4	30	-40	22	26	2800	6	+60.1
5[c]	10	0	22	28	2500	5	+36.0

a. Monomer 200 mg was dissolved in 1 mL of CH_2Cl_2, and polymerized using PF_5 as initiator. b. Determined by GPC with polystyrene as a standard. c. Trifluoromethanesulfonic acid was used as the initiator.

and aluminum chloride. The regioselectivity of the cleavage of benzylidene acetals was previously reported by Lipták.[7] The regioselectivity depends on the stereochemistry of the starting benzylidene acetal: for the endo isomer, the reducing agent attacks the equatorial oxgen atom, affording an equatorial hydroxyl group. In this paper, 2-equatorial oxgen atom of **3** was reduced, because the benzylidene acetal of **3** was the endo isomer. By the reaction of **4** with trifluoromethanesulfonic anhydride, an equatorial trifluoromethanesulfonyloxy group was introduced at C-2, and then the configuration at C-2 was inverted from the *manno* to the *gluco* structure by an S_N2 substitution reaction with potassium phthalimide, producing 1,6-anhydro-2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-β-D-glucopyranose (**5**).

Ring-Opening Polymerization. Compound **5** was polymerized under cationic conditions at high vacuum. The molecular weights of the obtained components were estimated by GPC using G3000HXL, G2000HXL, and G1000HXL columns. As shown in Table 1, polymerization of **5** yielded oligomers having a number average degree of polymerization from 5 to 7. The ^{13}C NMR spectra of the oligomers showed a single C1 peak at 97.5 ppm (Figure 1), indicating stereoregular oligosaccharides. When 2-deoxy-2-phthalimido-β-D-glucopyranose derivatives are used as glycosyl donors of glycosylation reactions, the β-linkage is generally formed, presumably due to the steric hindrance by the 2-phthalimido residue. The C1 signals of various 2-deoxy-2-phthalimido-β-D-glucopyranose derivatives appear between 97 and 98 ppm.[8,9,10] The main component of **7** (No. 3 of Table 1) was purified by silica gel chlomatography and its ^1H NMR spectrum showed an anomeric proton signal at 5.21ppm with a large coupling constant $J_{1,2}$=7.92 Hz. The large $J_{1,2}$ value means that the configuration

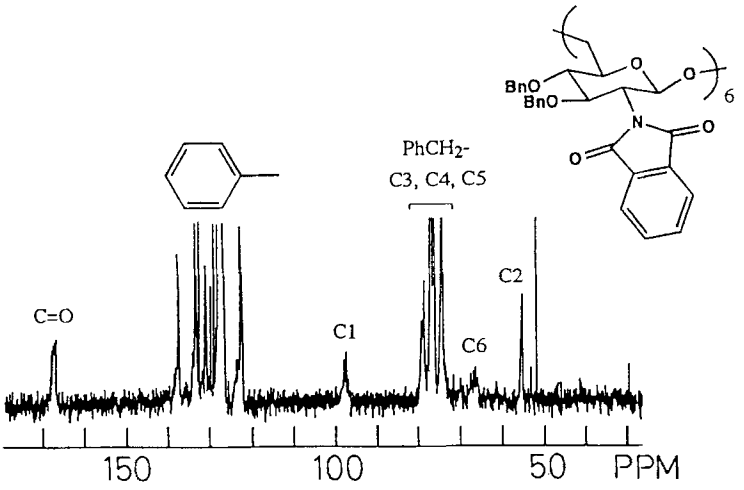
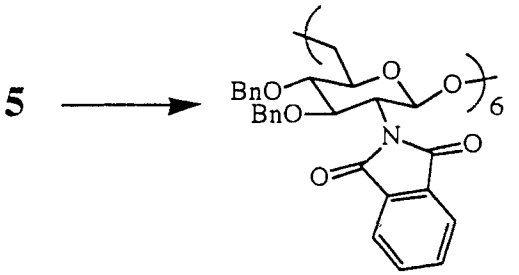


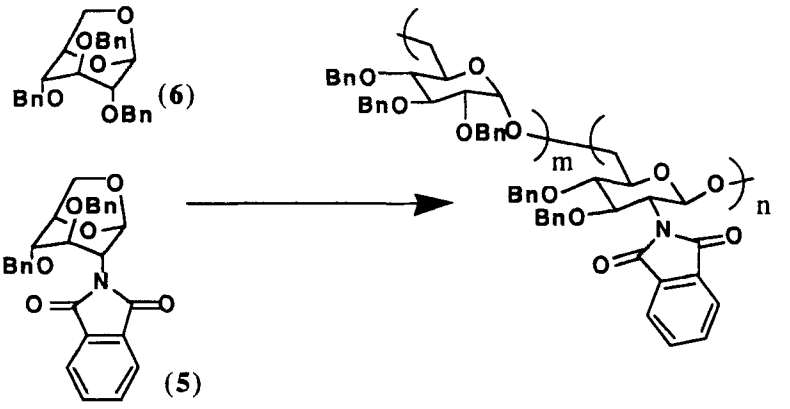
Figure 1. ^{13}C NMR spectrum of 2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-(1→6)-β-D-glucopyranan.

between H-1 and H-2 proton is *anti*. From the $J_{1,2}$ value, chemical shifts of the anomeric carbons, and the optical rotation of the synthetic oligomers, it was concluded that the oligomers were 2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-(1→6)-β-D-glucopyranan, as shown in Scheme 2. From the ^{13}C NMR spectrum of the main conponent, the integral ratio between intra-chain C6 and C6 of nonreducing terminal indicated that the degree of polymerization was 5.1 (from the GPC measurement, the degree of polymerization was 6.0 as shown in Table 1).



Scheme 2. Polymerization of **5**.

Copolymerization of 5 with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose. As shown in Scheme 3, it was attempted to copolymerize **5** with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**6**). The copolymerizations were carried out at -40 °C using 10 mol% of PF_5 as an initiator. The mole fraction of **5** in copolymers was determined by ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum of the obtained copolymer, the C1 peak of the glucosamine monomer unit appearing at 97.5 ppm can be easily distinguished from the anomeric carbon signal of the tri-*O*-benzyl glucose monomer unit (97.8 ppm). The mole fraction of the glucosamine monomer unit was



Scheme 3. Copolymerization of **5** with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**6**).

Table 2. Copolymerization of **5** and **6**.[a]

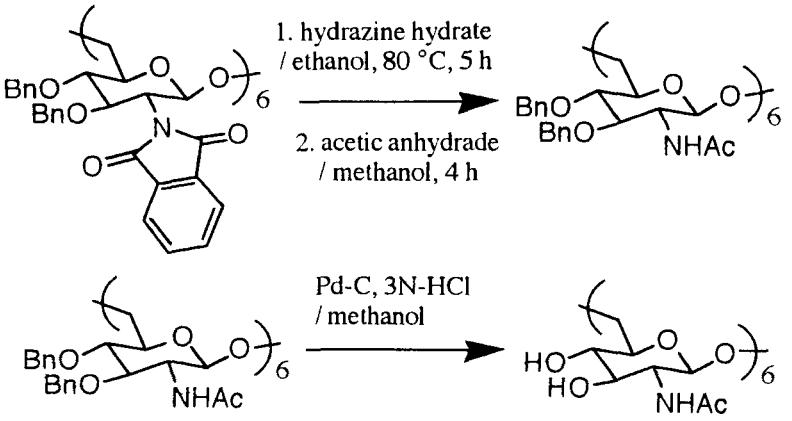
No.	Time, min.	mole fraction of **5** in feed / in copolymer,[b] %	Yield, %	$\overline{M}_n$[c] X10^3	$\overline{M}_w / \overline{M}_n$	$[\alpha]_D^{13}$, deg.
1	1320	100 / 100	26.0	2.8	1.15	+60.1
2	120	89.2 / 48.1	10.3	3.5	1.03	+66.0
3	105	76.7 / 47.5	18.3	6.4	1.32	+70.4
4	60	43.3 / 32.1	30.5	8.8	1.56	+88.0
5	45	23.4 / 17.0	54.9	22.9	1.90	+104.8
6	30	9.3 / 8.4	51.0	20.5	1.89	+116.4
7	30	0 / 0	75.5	34.6	1.49	+113.4

a. Solvent, CH_2Cl_2, 1 mL; initiator, PF_5, 10 mol%; temp., -40°C.
b. Estimated by ^{13}C NMR.
c. Estimated by GPC using polystyrene standard.

estimated from the relative intensities of the C1 signals from both components. These data agreed with those from elemental analysis. As shown in Table 2, **5** was efficiently incorporated into polymer chains. From the copolymerization data, the monomer reactivity ratios were calculated by the Kelen-Tüdös method.[11] Monomer reactivity ratios

are defined as $r_5=k_{55}/k_{56}$, $r_6=k_{66}/k_{65}$, where k_{55} shows the reaction rate constant of **5** against the propagating end derived from **5**. The calculated monomer reactivity ratios were $r_5=0.0214$ and $r_6=1.06$, indicating that the reactivity of **5** is as high as **6** against the highly-reactive cation derived from **6**, while it is low against the cation derived from **5**. That is to say, although nucleophilicity of anhydro-ring oxgen of both monomers are high, the reactivity of **5** is lower than **6** against the propagating chain end derived from **5**. The difference between **5** and **6** is the substituent at C-2, i.e., phthalimido and benzyloxy groups. The result showed that the reaction of **5** with the **5** derived cation was restricted by steric hindrance of whole propagating oligosaccharide chain end of **5** and phthalimido groups of **5**, like a mismatched pair.[13]

Deprotection of Polymers. Dephthaloylation of 2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-(1→6)-β-D-glucopyranan (**7**) was carried out by hydrazine hydrate in ethanol. *N*-acetylation using acetic anhydride in methanol gave 2-acetamido-2-deoxy-3,4-di-*O*-benzyl-(1→6)-β-D-glucopyranan (**8**). In the IR spectrum of **8**, the absorption at 1710 cm^{-1} assigned to the imide group, disappeared and a 1680 cm^{-1} signal, assigned to the amide group, newly appeared. Debenzylation was carried out by catalytic hydrogenation in the presence of 10% Pd-C in methanol to give novel 2-acetamido-2-deoxy-(1→6)-β-D-glucopyranan (**9**). In the IR spectrum of **9**, absorptions at 700 and 750 cm^{-1}, assigned to benzyl groups of **8**, were absent. Dephthaloylation and debenzylation were confirmed also by NMR spectroscopy. The ^{13}C NMR spectrum of **9** in D_2O showed a single C1 peak at 101.4 ppm. Klaus Bock et al. has provided a collection of ^{13}C NMR spectra of various oligosaccharides. Their article also showed the chemical shifts about C1 of *N*-acetyl-α- and β-D-glucosamine components. For example, on the GlcNAc-β-(1→6)-GlcNAc-α-(1→4)-Gal, C1 signals of α and β-GlcNAc appears at 101.9 and 98.6 ppm, respectively, and 101.4 ppm was suitable to be identified with β-linkage.[14]



Scheme 4. Deprotection of 2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-(1→6)-β-D-glucopyranan.

EXPERIMENTAL

General Methods. 270-MHz ^{1}H NMR spectra were measured in $CDCl_3$ or CD_3OD (for compound **8** and **9**) using tetramethylsilane as internal reference and employing a JEOL EX-270 spectrometer. Optical rotations were measured in $CHCl_3$ with a digital polarimeter. Gel-permeation chromatography was carried out with a Shimadzu LC-9A chromatograph using GPC-802, 803, and 804 columns and a Toso CCPD chromatograph using G3000HXL, G2000HXL, and G1000HXL columns.

1,6-Anhydro-2,3-*O*-(*S*)-benzylidene-β-D-mannopyranose (2). 1,6-Anhydro-β-D-mannopyranose (**1**, 5.0 g, 30.9 mmol), prepared from D-mannopyranose by the method of Fraser-Reid,[12] was dissolved in dry dimethylformamide (20 mL). α,α'-Dimethoxytoluene (30 mL, 209 mmol) and *p*-toluenesulfonic acid (0.6 g, 3.15 mmol) were added to the solution and the reaction mixture was stirred at 50 °C for 1 h under anhydrous conditions. The residue was dissolved in chloroform (200 mL), neutralized with triethylamine, and successively washed with water. Crystallization of **2** was effected from ethanol: 5.02 g, 65.2 %; $[\alpha]_D^{21}$ -44.6°(*c* 1.0, $CHCl_3$), ^{1}H NMR: 3.86 (t, 1H, $J_{5,6}$ = 7.59 Hz, $J_{6,6'}$ = 6.26 Hz, H6), 4.07 (t, 1H, $J_{4,5}$ = 1.32 Hz, H4), 4.09 (t, 1H, $J_{2,3}$ =1.98 Hz, H2), 4.21 (t, 1H, H3), 4.25 (t, 1H, $J_{5,6'}$ = 0.99 Hz, H6'), 4.60 (m, 1H, H5), 5.51 (s, 1H, H-1), 5.77 (s, 1H, H_{CHPh}), 7.41 (q, 4H, H_{Ph}), 7.65 (s, 1H, H_{Ph}), elemental analysis (Calcd.; C 62.39 %, H 5.65 %, Found; C 61.15 %, H 5.64 %).

1,6-Anhydro-4-*O*-benzyl-2,3-*O*-(*S*)-benzylidene-β-D-mannopyranose (3). A solution of 1,6-anhydro-2,3-*O*-(*S*)-benzylidene-β-D-mannopyranose (**2**, 5.04 g, 20.2 mmol) in dimethylformamide (50 mL) was added dropwise to a suspension of sodium hydride (1.93 g, 80.5 mmol) in dimethylformamide (150 mL) at 20 °C over a period of 5 h. After stirring for an additional hour, benzyl chloride (5.12 mL, 44.5 mmol) in dimethylformamide (45 mL) was added to the mixture. The reaction mixture was stirred for 16 h, and quenched by adding methanol. The residue was extracted with 1 L of chloroform, and the chloroform layer was repeatedly washed with water. Crystallization of **3** was achieved from a solution of ethanol: 6.45 g, 93.9%; $[\alpha]_D^{21}$ -41.8° (*c* 1.0, $CHCl_3$), ^{1}H NMR : 3.78 (s, 1H, H-4), 3.83 (d, 1H, H-6'), 3.95 (d, 1H, $J_{6,6'}$ = 7.26 Hz, H-6), 4.26 (d, 1H, H-2), 4.28 (d, 1H, $J_{2,3}$ = 6.93 Hz, H-3), 4.66 (m, 1H, H-5), 4.67, 4.75 (d, 2H, *J* 12.2, $-CH_2Ph$), 5.52 (d, 1H, $J_{1,2}$ = 2.97 Hz, H-1), 5.76 (s, 1H, O_2CHPh), 7.38, 7.39 (s, 10H, Ph), elemental analysis (Calcd.; C 70.56 %, H 5.93 %, Found; C 70.67 %, H 6.07 %).

1,6-Anhydro-3,4-di-*O*-benzyl-β-D-mannopyranose (4). 1,6-Anhydro-4-*O*-benzyl-2,3-*O*-(*S*)-benzylidene-β-D-mannopyranose (**3**, 6.45 g, 19.0 mmol) was dissolved in a suspension of lithium aluminum hydride (0.735 g, 19.4 mmol) in a mixture of dichloromethane (50 mL) and diethyl ether (150 mL). Aluminum chloride

(2.58 g, 19.4 mmol) was added and the reaction mixture was stirred at 40 °C for 30 min. The residue was cooled to room temperature and the reaction was quenched by careful addition of water. The residue was dissolved in chloroform, and the chloroform solution was washed with water, dried, and concentrated. The residue was chromatographed on silica gel (hexane : ethyl acetate = 2 : 3 as eluent) to purify **4**, which was crystallized from a syrup: 3.96 g, 60.6%; $[\alpha]_D^{21}$ -58.3° (*c* 1.0, $CHCl_3$), ^1H NMR: 3.49 (s, 1H, H-4), 3.69 (dd, 1H, $J_{5,6}$ = 5.94 Hz, $J_{6,6'}$ = 6.93 Hz, H-6), 3.73 (q, 1H, H-2), 3.78 (m, 1H, H-3), 4.07 (dd, 1H, $J_{5,6'}$ = 0.99 Hz, H-6), 4.50-4.55 (m, 5H, H-5, $-CH_2Ph$), 5.35 (s, 1H, H-1), 7.34 (10H, Ph), elemental analysis (Calcd.; C 70.15 %, H 6.49 %, Found; C 69.70 %, H 6.70 %).

1,6-Anhydro-2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-β-D-glucopyranose (5). To a cooled (-10 °C) solution of 1,6-anhydro-3,4-di-*O*-benzyl-β-D-mannopyranose (**4**, 1.2 g, 3.51 mmol) in dichloromethane (6 mL), trifluoromethanesulfonic anhydride (1.2 mL) and pyridine (0.7 mL) in dichloromethane (26 mL) were added under a nitrogen atmosphere. After raising the temperature to 0 °C, the reaction mixture was stirred for 2 h. The residue was extracted with chloroform and the solution was washed with water. After concentration of the organic layer, a crude syrup containing 1,6-anhydro-3,4-di-*O*-benzyl-2-*O*-trifluoromethanesulfonyl-β-D-mannopyranose was obtained. The syrup was dissolved in dimethylformamide (10 mL). After adding potassium phthalimide (5.0 g), the reaction mixture was vigorously stirred to maintain a well dispersed mixture. After 2 days, the mixture was diluted with chloroform and filtered. The filtrate was washed with water and chromatographed on silica-gel (benzene : ethyl acetate = 2 : 3). Compound **5** was crystallized from diethyl ether and recrystallizated from the same solvent: 326mg, 21.9%; $[\alpha]_D^{22}$ +31.4° (*c* 1.0, $CHCl_3$), ^1H NMR: 3.62 (d, 1H, $J_{3,4}$ = 6.93 Hz, H-4), 3.73 (dd, 2H, H-6, H-6'), 4.06 (d, 1H, $J_{2,3}$ = 9.89 Hz, H-2), 4.19 (dd, 1H, H-3), 4.62 (dd, 2H, $J_{3,4}$ = 11.87 Hz, $-CH_2Ph$), 6.65 (m, 1H, H-5), 4.70 (dd, 2H, $J_{3,4}$ = 11.88 Hz, $-CH_2Ph$), 5.46 (s, 1H, H-1), 7.39 (m, 14H, H_{Ph}), ν 1710 cm^{-1} (imido), elemental analysis (Calcd.; C 71.32 %, H 5.35 %, N 2.97 %, Found; C 71.65 %, H 5.39 %, N 2.91 %).

Ring-opening polymerization of 1,6-Anhydro-2-deoxy-3,4-di-*O*-benzyl-2-phthalimido-β-D-glucopyranose (5). Ring-opening polymerization of **5** was carried out using phosphorus pentafluoride as an initiator under high vacuum. After the polymerization was quenched with methanol, the polymer solution in chloroform was neutralized with aqueous sodium bicarbonate, and washed with water. The oligomer (**7**) was purified by reprecipitation using the chloroform-methanol system, and obtained by freeze-drying from benzene solution.

Copolymerization of 5 with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (6). Copolymerizations of **5** with **6** were carried out using 10 mol %

of phosphorus pentafluoride as initiator at -40 °C. The reactions were terminated with methanol, and polymers were purified according to the same way for purification of **7**.

2-Acetamido-2-deoxy-3,4-di-*O*-benzyl-(1→6)-β-D-glucopyranan (8). 2-Deoxy-3,4-di-*O*-benzyl-2-phthalimido-(1→6)-β-D-glucopyranan (**7**, 200 mg) was suspended in 20 mL of ethanol containing 5 mL of hydrazine hydrate. The reaction mixture became a clear solution at 80 °C, which was stirred for 5 h. The reaction mixture was concentrated under reduced pressure to give a syrup. The syrup was dissolved in a mixture of methanol (20 mL) and acetic anhydride (10 mL), and stirred at room temperature for 1 h. The reaction mixture was poured into cold aqueous $NaHCO_3$ and extracted with chloroform. The chloroform layer was washed with water, dried over sodium sulfate, and concentrated under reduced pressure. 2-Acetamido-2-deoxy-3,4-di-*O*-benzyl-(1→6)-β-D-glucopyranan (**8**) was purified by reprecipitating three times using the chloroform-ether system: 149 mg, 91.4 %; ν 1650 cm^{-1} (N-H), ν 1680 cm^{-1} (C=O), ν 700 cm^{-1} and ν 750 cm^{-1} (phenyl group).

2-Acetamido-2-deoxy-(1→6)-β-D-glucopyranan (9). A mixture of 2-acetamido-2-deoxy-3,4-di-*O*-benzyl-(1→6)-β-D-glucopyranan (**8**, 100 mg) and 10% Pd-C (120 mg) in methanol (30 mL), and 3N HCl (2 μL) was shaken under a hydrogen atmosphere for 8 days at room temperature. The residue was filtered off and the filtrate was concentrated. 2-Acetamido-2-deoxy-(1→6)-β-D-glucopyranan (**9**) was purified by reprecipitation using the methanol-ethyl acetate system. Then **9** was obtained by freeze-drying from water solution: 24 mg, 45.3 % ; $[\alpha]_D^{29}$ +6.50° (*c* 1.0, $CHCl_3$), ν 1650 cm^{-1} (N-H), ν 1680 cm^{-1} (C=O).

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