N-Glycosylation Approach to Glucose-Functionalized Diamine and Its Use for Protection-Free Synthesis of Polyurea Bearing Glucoside Pendant

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ABSTRACT: A glucose-functionalized diamine was prepared and used as a new monomer for polyurea synthesis. The diamine was prepared by *N*-glycosylation of 1,6-hexamethylenediamine with D-glucose. Upon adding diisocyanates to the diamine, isocyanate reacted selectively with the amino groups, not with the hydroxyl groups of the glucose-derived structure, to give the corresponding polyureas. The polyureas exhibited highly hydrophilic nature due to the presence of the glucose-derived side chain. A ternary system consisting of the glucose-functionalized diamine, piperazine, and diisocyanate gave the corresponding polyureas, where content of the glucose-derived moiety was tunable by feed ratio between the diamine and piperazine. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 51: 298–304, 2013

KEYWORDS: D-glucose; hydrophilic polymers; *N*-glycosylation; renewable resources; step-growth polymerization

INTRODUCTION Monosaccharides are attractive building blocks for synthesizing various polymer materials.[1–6] They possess plural hydroxyl groups, of which regioselective reactions permit incorporation of monosaccharide-derived structures into materials in well-defined manners, so that those materials inherit various virtues such as affinity to biomolecules, hydrophilicity, and self-assembling nature from monosaccharides.[7–11] In addition, those hydroxyl groups are located in specifically defined orientations, and thus efficient use of them will lead to precise construction of three dimensional macromolecular architectures.[12,13] Monosaccharides have another important reactive site, that is, the anomeric position, to which various functional groups can be introduced.[14] *N*-Glycosides are a class of compounds synthesized by introduction of amines to the anomeric position of monosaccharides. So far, they have attracted much attention due to their bioactivity,[15–18] molecular recognition,[19] and their potential applicability to surfactants.[20–22] *N*-glycosides can be synthesized quite simply, just by mixing monosaccharides and the corresponding amines in bulk or in alcohol solutions. This simple method as well as the structural diversity of amines has prompted the development of functional *N*-glycoside derivatives.

The focus of the present work is utilization of *N*-glycosides as a new class of monosaccharide-derived monomers. More specifically, our interest is exploitation of *N*-glycosylation as a convenient method for modifying amines into "sugar-functionalized" amine-type monomers. Diamines are highly important monomers for polymer synthesis based on their reactions with electrophilic molecules involving isocyanates, epoxides, and acrylates that afford practically important class of polymers such as polyureas, polyamines, and polyaminoesters. Modification of diamines by *N*-glycosylation can afford the corresponding "sugar-functionalized" amines, of which utilization as new monomers for polymer synthesis will open a new window for development of sugar-functionalized polymers with unique properties. So far, sugar-functionalized diamines have been synthesized,[23,24] and their biological activity[25–27] and ability to form metal complexes[28,29] have been evaluated; however, to the best of our knowledge, there have been no reports on their application as monomers for polymer synthesis.

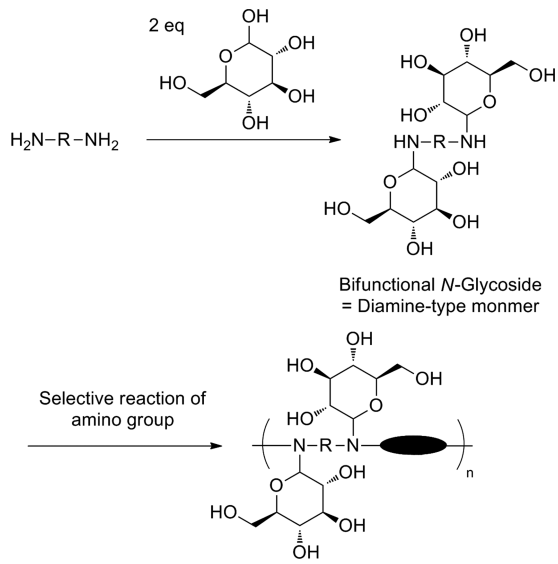
Herein, we report a polyaddition system with exploiting a bifunctional *N*-glycoside, which can be easily prepared by *N*-glycosylation of diamine with glucose (Scheme 1). In this system, protection of the glucose-derived hydroxyl group can be avoided based on the difference in intrinsic nucleophilicity between hydroxyl and amino groups, leading to the formation of polymers bearing glucose moiety in the side chain.

EXPERIMENTAL

Materials

D-Glucose (Glu), hexamethylenediamine (HMDA), butylamine, and lithium chloride were purchased from Kishida Chemical Co. and used as received. Phenyl isocyanate, methylenediphenyl

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 The concept of this work: modification of diamine with glucose and utilization of the modified diamine for polymer synthesis.

4,4′-diisocyanate (MDI), and 2,6-tolylenediisocyanate (TDI) were purchased from Tokyo Chemical Industry Co. and distilled prior to use. *N, N*-Dimethylformamide was purchased from Wako Pure Chemical Industries Co. and distilled prior to use. Other reagents and solvents were purchased from Wako Pure Chemical Industries Co. and used as received.

Instruments

NMR spectra (400 MHz for ^{1}H; 100.6 MHz for ^{13}C) were recorded on a JEOL NMR spectrometer model JNM-AL400. Chemical shift δ and coupling constant J are given in parts per million and Hertz, respectively. IR spectra were obtained on a JASCO FT/IR-470 and wave number ν is given in cm^{-1}. Number average molecular weight (M_n) and weight average molecular weight (M_w) were estimated by size exclusion chromatography (SEC), performed on a Tosoh chromatograph model HLC-8120GPC equipped with Tosoh TSK gel-Super HM-H styrogel columns (6.0 mm $\varphi \times$ 15 cm), using *N, N*-dimethylformamide (DMF) containing 1 wt% lithium bromide as an eluent at the flow rate of 0.6 mL/min after calibration with polystyrene standards. Thermogravimetric analysis (TGA) was performed with a SEIKO Instruments TG/DTA model EXSTAR6000 under nitrogen flow.

Synthesis of *N*-Butyl-*β*-glucopyranosylamine 1

To a suspension of Glu (18.02 g; 100.0 mmol) in methanol (8 mL), butylamine (10.97 g; 150.0 mmol) was added and heated at 60 °C for 30 min. Addition of hot ethanol (60 mL) to the solution and cooling to room temperature resulted in gelation of the mixture, and the gel was divided into small pieces. Toluene (30 mL) was added to the gel, and the mixture was stirred at room temperature, filtered with suction, washed with toluene, and then dried under vacuum to obtain **1** (17.37 g; 73.83 mmol, 74%) as a white powder.

^{1}H NMR (DMSO-d_6, δ): 4.83 (d, J = 4.9 Hz, 1H), 4.79 (d, J = 4.4 Hz, 1H), 4.45 (d, J = 3.9 Hz, 1H), 4.35 (t, J = 5.9 Hz, 1H), 3.66–3.61 (m, 2H), 3.43–3.35 (m, 1H), 3.14–3.06 (m, 1H), 3.15–3.08 (m, 2H), 2.89–2.81 (m, 1H), 2.82–2.75 (m, 1H), 2.13 (br s, 1H), 1.41–1.25 (m, 4H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d_6, δ): 90.78, 77.61, 77.44, 73.51, 70.54, 61.39, 45.19, 32.14, 19.93, 13.97.

Reaction of 1 with Phenyl Isocyanate

To a solution of **1** (0.941 g; 4.00 mmol) and lithium chloride (0.424 g; 10.0 mmol) in DMF (24 mL), phenyl isocyanate (0.476 g; 4.00 mmol) was added at 0 °C. The resulting solution was allowed to warm to room temperature and was stirred for 24 h. DMF was removed under reduced pressure, and the resulting residue was passed through a short pad of silica gel [eluent = ethyl acetate/methanol (4/1)] to remove a highly polar fraction. The corresponding adduct **2** thus obtained was used in the next reaction step without further purification. The characteristic spectroscopic data of **2** are as follows:

^{1}H NMR (DMSO-d_6, at 60 °C, δ): 8.30 (s, 1H), 7.46 (d, J = 8.3 Hz, 2H), 7.20 (t, J = 7.8 Hz, 2H), 6.92 (t, J = 7.3 Hz, 1H), 5.30 (br s, 1H), 4.95 (br s, 1H), 4.88 (d, J = 8.3 Hz, 2H), 4.41 (br s, 1H), 3.68 (d, J = 11 Hz, 1H), 3.57 (d, J = 11 Hz, 1H), 3.46–3.38 (m, 3H), 3.34–3.22 (m, 3H), 3.19 (br s, 1H), 3.11 (br s, 1H), 2.50 (s, 1H), 1.59–1.50 (m, 2H), 1.36–1.24 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (DMSO-d_6, at 60 °C, δ): 154.9, 139.9, 128.2, 121.3, 119.2, 86.17, 78.38, 70.72, 69.51, 60.51, 42.79, 31.10, 19.23, 13.31.

Acetylation of Hydroxyl Groups of 2

To a solution of crude **2** obtained as mentioned above in pyridine (20 mL), acetic anhydride (10 mL) was added and stirred at room temperature. After 24 h, the volatiles were removed under reduced pressure. The resulting residue was fractionated by silica gel column chromatography [eluent = hexane/ethyl acetate (1/1)] to obtain tetraacetate **3** (1.67 g; 3.20 mmol; 80% from **1**) as a white powder. IR (KBr): ν = 1756, 1674.

^{1}H NMR (DMSO-d_6, at 80 °C, δ): 8.12 (s, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.27 (t, J = 8.1 Hz, 2H), 7.00 (t, J = 7.3 Hz, 1H), 5.59 (d, J = 9.3Hz, 1H), 5.34 (t, J = 9.3 Hz, 1H), 5.23 (t, J = 9.3 Hz, 1H), 5.06 (t, J = 9.5 Hz, 1H), 4.17 (d, J = 4.4 Hz, 2H), 4.10–4.00 (m, 1H), 3.40–3.18 (m, 2H), 2.02 (s, 3H), 2.01 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.57–1.45 (m, 2H), 1.36–1.25 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (DMSO-d_6, at 60 °C, δ): 169.3, 168.9, 168.7, 168.5, 154. 1, 139.2, 127.8, 122.1, 120.2, 86.87, 78.32, 72.49, 68.29, 68.04, 61.59, 42.64, 31.06, 19.88, 19.83, 19.72, 19.03, 13.12.

One-Pot Model Reactions

A mixture of butylamine (0.228 g; 3.12 mmol), Glu (0.65 g; 3.6 mmol), triethylamine (0.40 mL; 3.0 mmol), and methanol (4 mL) was stirred at 60 °C for 20 min. The resulting solution was concentrated under reduced pressure. The residual white solid was dried under vacuum, and then dissolved in DMF (10 mL) containing lithium chloride (0.33 g; 7.8 mmol). To the solution, a solution of phenylisocyanate (0.372 g; 3.13 mmol) in DMF (5 mL) was added at 0 °C and stirred at room temperature under argon. After 12 h, pyridine (10 mL) and acetic anhydride (5 mL) were added successively, and the

solution was stirred at room temperature for 7 h. The volatiles were removed under reduced pressure, and the resulting residue was dissolved in ethyl acetate (20 mL). The resulting solution was washed with 10 mL of water three times, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was fractionated by silica gel column chromatography (eluent: hexane/ethyl acetate = 2/1) to obtain **3** (1.40 g; 2.68 mmol; 86%) as a white solid.

Synthesis of Polyurea 6a

To a solution of HMDA (0.305 g; 2.63 mmol) in methanol (10 mL), Glu (1.14 g; 6.33 mmol) and triethylamine (0.38 mL; 2.6 mmol) were added successively. The resulting mixture was stirred at 60 °C for 20 min. The volatiles were removed under reduced pressure to obtain a mixture of bifunctional *N*-glycoside **4** and Glu. To this mixture, lithium chloride (0.55 g; 13 mmol) and DMF (23 mL) were added and stirred for 30 min at room temperature. To the resulting solution, a solution of MDI (0.657 g; 2.63 mmol) in DMF (3 mL) was added and stirred at room temperature. After 12 h, pyridine (10 mL) and acetic anhydride (5 mL) were added and stirred at room temperature for 12 h. The resulting solution was concentrated under reduced pressure and diluted with methanol (20 mL). To this mixture, water (10 mL) was added to precipitate the target polymer **6a**. The resulting yellow precipitate was isolated by filtration with suction and dried under vacuum. The obtained solid was dissolved in ethyl acetate (50 mL) and the solution was poured into diethyl ether (200 mL). The resulting white precipitate was isolated by filtration with suction, dried under vacuum. This precipitation process with using ethyl acetate/ether was repeated once to obtain polymer **6a** (1.97 g; 70%). IR (KBr): ν = 1753, 1664.

Synthesis of Polyurea 6b

From HMDA (0.341 g; 2.93 mmol), Glu (1.27 g; 7.04 mmol), and TDI (0.522 g; 3.00 mmol), polyurea **6b** was synthesized and isolated according to the procedure described above for the synthesis of polyurea **6a**. As a result, polyurea **6b** (1.07 g; 38%) was obtained as a white solid. IR (KBr): ν = 1752, 1666.

Synthesis of Polyurea 8a

To a solution of HMDA (0.301 g; 2.59 mmol) in methanol (8 mL), Glu (0.65 g; 3.6 mmol) and triethylamine (0.30 mL; 2.1 mmol) were added successively. The resulting mixture was stirred at 60 °C for 20 min. The volatiles were removed under reduced pressure to obtain a mixture of bifunctional *N*-glycoside **4** and Glu. To this mixture, lithium chloride (0.55 g; 13 mmol), piperazine (PZ; 74.6 mg; 0.866 mmol) and DMF (35 mL) were added successively and stirred for 30 min at room temperature. To the resulting solution, a solution of MDI (0.864 g; 3.46 mmol) in DMF (3 mL) was added and stirred at room temperature. After 12 h, pyridine (10 mL) and acetic anhydride (5 mL) were added and stirred at room temperature for 12 h. The resulting solution was concentrated under reduced pressure and diluted with methanol (20 mL). To this mixture, water (10 mL) was added to precipitate the target polymer **8a**. The resulting yellow precipitate was isolated by filtration with suction and dried under vacuum. The obtained solid was dissolved in ethyl acetate (50 mL) and the solution was poured into diethyl ether (200 mL). The resulting white precipitate was isolated by filtration with suction, dried under vacuum. This precipitation process with using ethyl acetate/ether was repeated once to obtain polymer **8a** (2.11 g; 71%). IR (KBr): ν = 1744, 1662.

Synthesis of Polyurea 8b and Isolation of Its Precursor 7b

From HMDA (0.357 g; 3.07 mmol), Glu (1.33 g; 7.38 mmol), PZ (0.264 g; 3.07 mmol), and MDI (1.536 g; 6.14 mmol), polyurea **8b** was synthesized and isolated according to the procedure described above for the synthesis of polyurea **8a**. As a result, polyurea **8b** (2.51 g; 60%) was obtained as a pale yellow solid. IR (KBr): ν = 1658.

Polyurea **7b**, of which treatment with acetic anhydride and pyridine gave **8b**, was synthesized and isolated as follows: From HMDA (0.370 g; 3.19 mmol), Glu (1.38 g; 7.66 mmol), PZ (0.274 g; 3.19 mmol), and MDI (1.60 g; 6.37 mmol), polyurea **7b** was synthesized according to the procedure described above for the synthesis of polyurea **8a**. The resulting solution of **7b** in DMF (50 mL) was poured into water (300 mL). The resulting viscous precipitate was isolated by decantation and dried under vacuum at 85 °C for 10 days to give **7b** (2.54 g, 78%) as a pale yellow solid. IR (KBr): ν = 1755, 1659.

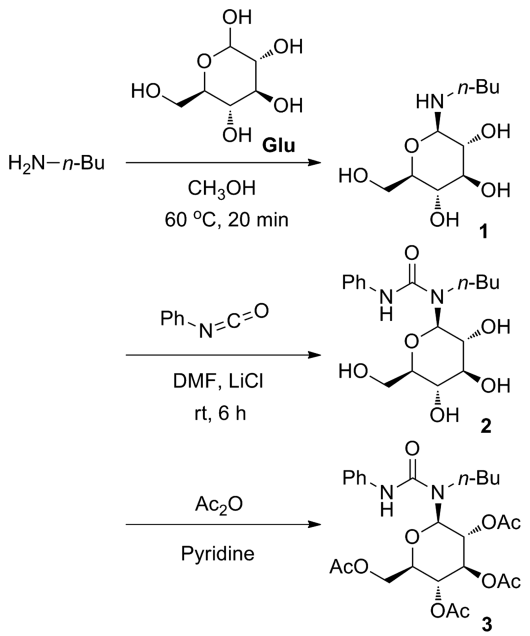
Synthesis of Polyurea 9

To a solution of PZ (0.258 g; 3.00 mmol) in DMF (10 mL), a solution of MDI (0.751 g; 3.00 mmol) in DMF (5 mL) was added, and the resulting solution was stirred at room temperature. After 12 h, the mixture became a gel. With using 60 mL of DMF, the formed gel was transferred into a 500-mL flask, and ethyl acetate (400 mL) was added to it. The resulting precipitate was isolated by filtration with suction and dried under vacuum to obtain polyurea **9** (0.979 g, 97%). IR (KBr): ν = 1642.

RESULTS AND DISCUSSION

Model System

As a model system for the designed polyaddition, we investigated a sequence of reactions starting from butylamine (Scheme 2). *N*-glycoside **1** was readily obtained by the *N*-glycosylation of butylamine with D-glucose (Glu) according to the reported procedure for the selective synthesis of β-isomer of *N*-glycosides.[21] Supporting Information Figures S1 and S2 show ^{1}H and ^{13}C NMR spectra of **1**, respectively. The obtained *N*-glycoside **1** was treated with an equimolar amount of phenyl isocyanate in DMF at room temperature. Addition of lithium chloride was quite effective to enhance the solubility of **1**, as is often the case with polysaccharide chemistry. After 6 h, the mixture was analyzed by TLC to confirm the complete consumption of **1** as well as formation of a UV-detectable compound as a sole product. This product was passed through a short silica gel column and analyzed by NMR. The resulting spectra are shown in Supporting Information Figure S3. These spectra confirmed the successful formation of compound **2** by the reaction of the amino group of **1** with phenyl isocyanate. The absence of any



SCHEME 2 A cascade of model reactions.

byproducts implied that phenyl isocyanate reacted with the amino group exclusively, without reacting with the hydroxyl groups of **1**. There have been a few reports on similar reactions of *N*-glycosides and isocyanates with high *N*-selectivity.[30–32] In addition, selective *N*-acylation of *N*-glycosides with acyl halide or acid anhydride have been also reported.[17,20,21]

For further detailed analysis of the adduct **2**, it was treated with acetic anhydride and pyridine to convert it into the corresponding tetraacetate **3**. Figures 1(a) and 2(a) show the ^{1}H and ^{13}C NMR spectra, respectively, where all the signals were completely assigned to all the protons and carbon atoms that constitute **3**. The assignment was made concrete by its ^{13}C NMR analysis with distortionless enhancement by polarization transfer with 135° pulse (DEPT135), ^{1}H–^{1}H correlation spectroscopy (HH-COSY), and ^{13}C–^{1}H correlation spectroscopy (CH-COSY). The resulting spectra are shown in Supporting Information Figures S4–S6. The IR spectrum of **3** indicated two strong absorptions at 1756 and 1674 cm^{-1}, which were attributable to ester C=O and urea C=O, respectively.

Next, the abovementioned reaction sequence was performed in one pot. *N*-glycoside **1** was prepared by treating butylamine with a slightly excess amount of Glu in methanol, followed by concentration under reduced pressure and drying under vacuum. The resulting mixture of **1** and Glu was dissolved in DMF with the aid of addition of lithium chloride, then phenylisocyanate was added to the solution. TLC analysis of the reaction mixture confirmed selective formation of **2**, which implied reaction of phenyl isocyanate with the hydroxyl groups of **1** and Glu was negligible. The final step

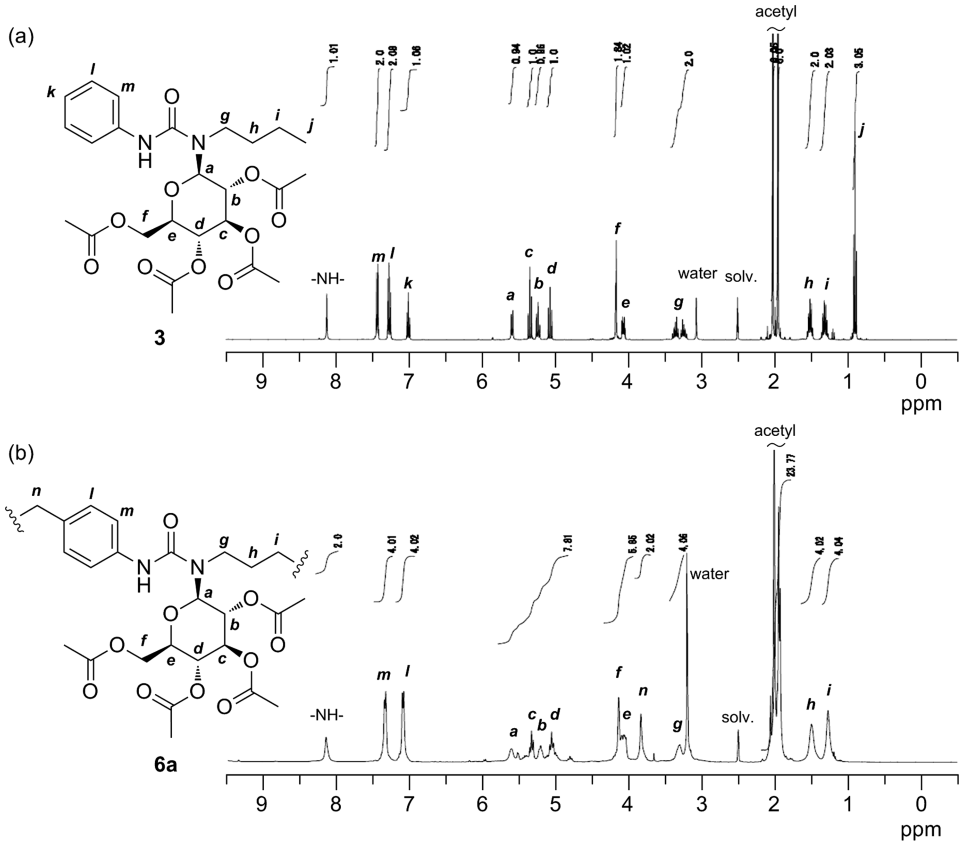


FIGURE 1 ^{1}H NMR spectra (in DMSO-d_6 at 80 °C) of model compound 3 and polyurea 6a.

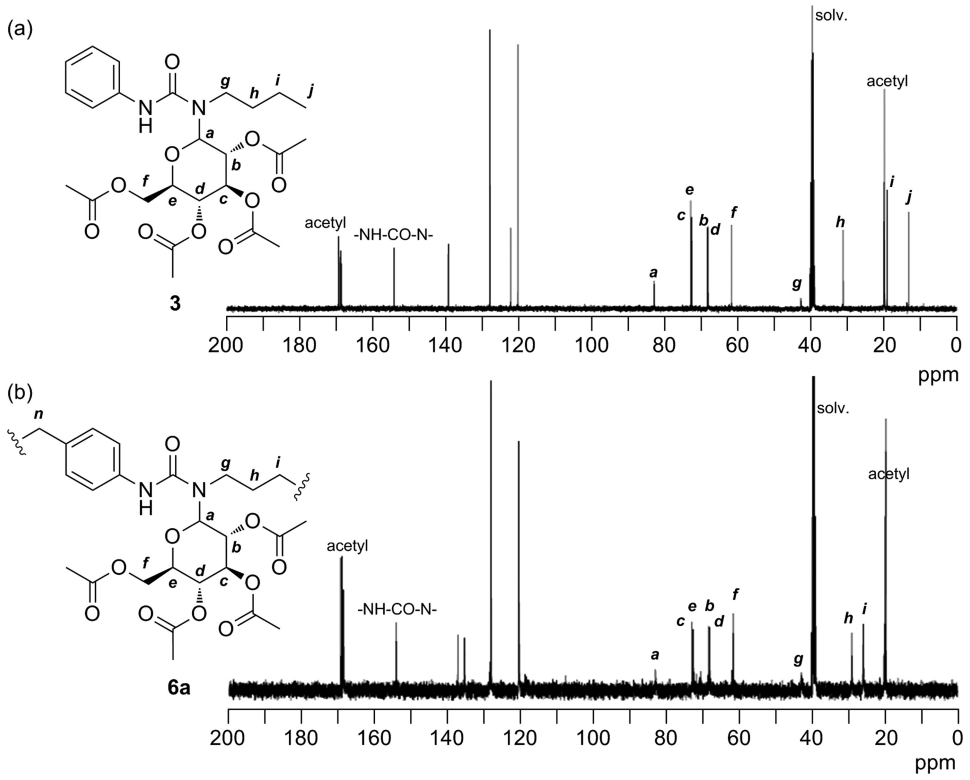
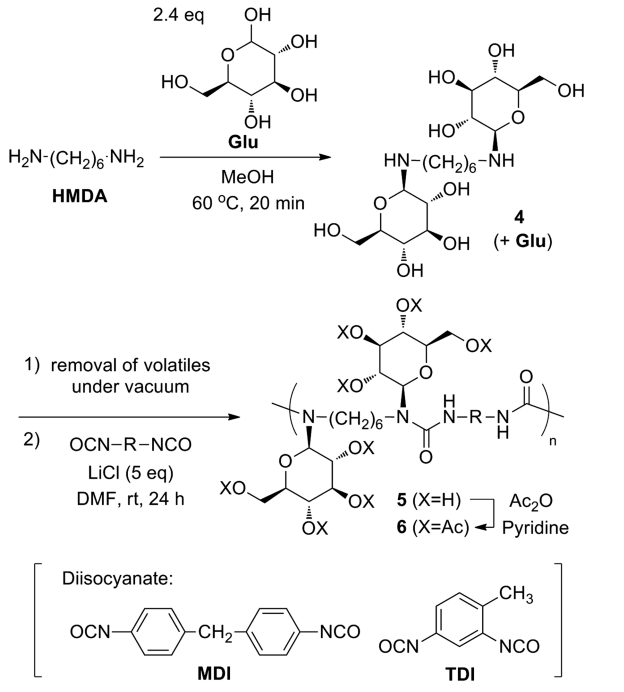


FIGURE 2 ^{13}C NMR spectra (in DMSO-d_6 at 80 °C) of model compound 3 and polyurea 6a.

was acetylation of the hydroxyl groups with acetic anhydride and pyridine, which gave **3** and D-glucose pentaacetate. These two products were separated by column chromatography leading to the successful isolation of **3** in 86% yield.

Polyaddition System

The high selectivity and efficiency demonstrated in the model system prompted us to perform the corresponding polyaddition system consisting of a bifunctional *N*-glycoside **4** and diisocyanate (Scheme 3). What we expected was an exclusive reaction of isocyanate with the amino groups of **4** that affords a linear polyurea **5** without contamination of its structure by reaction of isocyanate with the hydroxyl groups. A similar polyurea synthesis with using 2,6-diamino-2,6-dideoxy-D-glucose as a diamine-type monomer has been reported.[33] A bifunctional *N*-glycoside **4** was prepared just by mixing HMDA with Glu in a 1:2 molar ratio in methanol. The details of the preparation and isolation of **4** are described in Supporting Information. It was characterized by ^1H and ^{13}C NMR (Supporting Information Figures S1 and S2, respectively). These spectra clarified **4** was contaminated by a significant amount of methanol, presumably due to the high polarity of **4**. Heating **4** under vacuum to remove methanol completely resulted in gradual decomposition of **4**. To avoid this problematic issue, we decided to prepare **4** *in situ* and use it without further purification: HMDA and Glu were mixed in a 1:2.4 molar ratio, to ensure the complete modification of the amino groups. The resulting mixture of **4** and Glu was dried under vacuum, dissolved in DMF containing lithium chloride, and then treated with MDI (Table 1, Entry 1). During the polymerization, the system remained homogeneous throughout, suggesting that the target linear polyurea **5a** was formed without its crosslinking due to the reaction of the side chain hydroxyl groups with MDI. We attempted precipitation of **5a** from water to remove lithium chloride;



SCHEME 3 Synthesis of polyureas with using glucose-modified diamine 4.

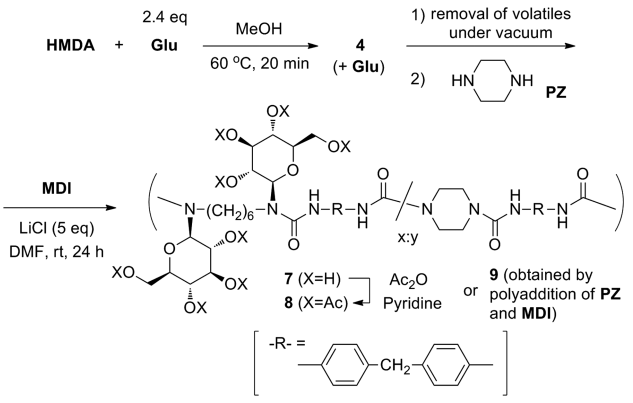
TABLE 1 Polyaddition of Bifunctional *N*-Glycoside **4** and Diisocyanate with Using PZ as a Comonomer

Entry	Diisocyanate	$[\mathbf{4}]_0$:$[\mathbf{PZ}]_0$	Polymer	Yield (%)[a]	Composition (**4**-Derived Unit: **PZ**-Derived Unit)[a]	M_n (M_w/M_n)[b]
1	MDI	100:0	**6a**	70	–	6300 (1.87)
2	TDI	100:0	**6b**	38	–	2940 (1.76)
3	MDI	75:25	**8a**	71	5:5	8870 (3.39)
4	MDI	50:50	**8b**	60	3:7	8060 (2.47)
5	MDI	0:100	**9**	97	–[c]	–[c]

[a] Determined by ^{1}H NMR.
[b] Estimated by SEC (eluent = DMF containing 1 wt % lithium bromide, PSt-standards).
[c] Not determined because of the insolubility of **9**.

however, addition of the DMF solution of **5a** to an excess amount of water led to emulsification, presumably due to the amphiphilicity of **5a**. To avoid such difficulty in isolation of **5a**, it was treated with acetic anhydride and pyridine to convert the hydroxyl groups into less polar acetate. The resulting polymer **6a** became immiscible with water and thus easily isolated by precipitation from water. The isolated **6a** was further purified by precipitation from ether. Figures 1(b) and 2(b) show the ^{1}H and ^{13}C NMR spectra of **6a**, which clarified the structural similarity between the repeating unit of **6a** and the model compound **3**. The IR spectrum of **6a** indicated two strong absorptions at 1753 and 1664 cm^{-1}, which were attributable to ester C=O and urea C=O, respectively. By SEC, the number average molecular weight (M_n) and weight average molecular weight (M_w) of **6b** were estimated to be 6300 and 11,800, respectively. In a similar way, polyaddition of **4** and tolylene-2,4-diisocyanate (TDI) was performed (Table 1, Entry 2). The resulting polymer was treated by acetic anhydride and pyridine, and thus the corresponding polyurea **6b** was obtained successfully.

Upon succeeding in the utilization of the sugar-modified diamine **4** for polyurea synthesis, we examined synthesis of polyureas with controlling content of the D-glucose-derived structure by employing PZ as a comonomer (Scheme 4). The reason why PZ was chosen from a wide variety of conventional diamines was that PZ is a secondary diamine that should exhibit similar reactivity to those of a secondary diamine **4** leading to statistic compositions of copolymers. Diamine **4**, prepared by the abovementioned procedure, was mixed with PZ in feed ratios in 75:25 and 50:50, and these diamine mixtures were dissolved in DMF containing lithium chloride and treated with MDI to perform polyaddition (Table 1, entries 3 and 4). The polyureas **7a** and **7b** formed *in situ* were converted into **8a** and **8b**, respectively, by acetylation of the hydroxyl groups. These polymers were isolated by precipitation from water. The compositions were determined by ^{1}H NMR. As a typical example, the spectrum of **8b** is shown in Figure 3. The signals attributable to the MDI-derived structures and those attributable to the **4**-derived structures were observed. By comparing the intensities of these signals, the degrees of introduction of **4**-derived component were calculated. The resulting values were lower than those expected from the feed ratios, implying that the reaction of the amino groups of **4** with isocyanate was sterically more hindered than that of PZ, presumably due to the presence of bulky glucose-derived moieties. Isolation of polyurea **7a** by precipitation from water was not successful due to emulsification, while polyurea **7b** with a smaller content of **4**-derived unit was isolated by precipitation from water successfully. As can be expected from the presence of plural hydroxyl groups in the side chain, **7b** was hygroscopic and thus removal of water from it by vacuum drying was not easy. Besides the copolymerizations, polycondensation of PZ



SCHEME 4 Synthesis of polyureas based on 4-PZ-MDI ternary system.

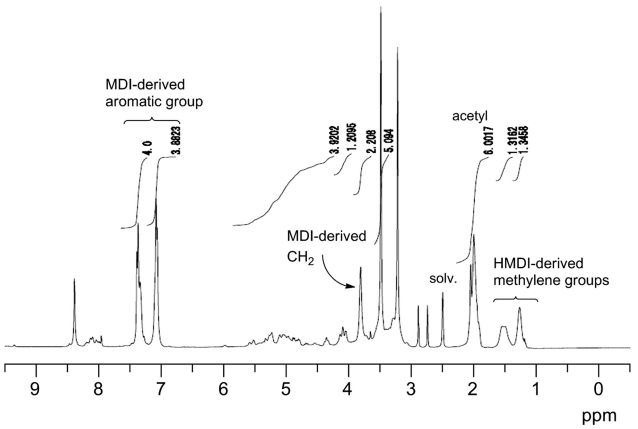


FIGURE 3 ^{1}H NMR spectrum of 8b.

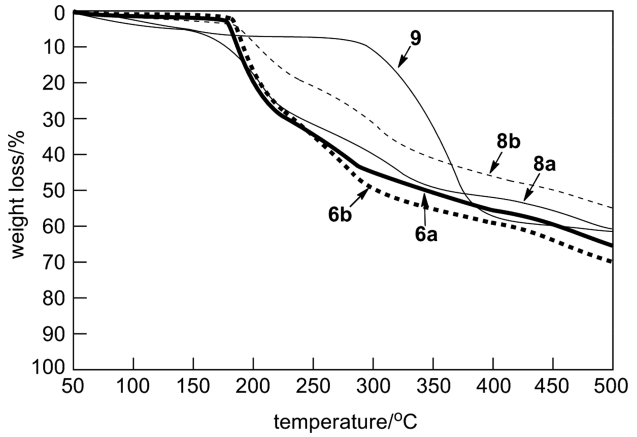


FIGURE 4 TG-profiles of the polyureas 6, 8, and 9.

and MDI was performed to obtain the corresponding polyurea **9** (Table 1, Entry 5).

Properties of Polyureas

The polyureas **6a, 6b, 7b, 8a**, and **8b** were soluble in DMSO and DMF containing lithium chloride, while they were insoluble in water, methanol, DMF, tetrahydrofuran, acetone, ethyl acetate, and ether. Polyurea **9** was insoluble in water and all the organic solvents tested for the other polyureas.

Thermal stability of the polyureas was investigated by TGA. The resulting profiles are shown in Figure 4. The profiles of **6a** and **6b** were similar to each other, as can be expected from the structural similarity. The profiles of **8a** and **8b** clarified that they were thermally more stable than **6a**. Polyurea **9** obtained by polyaddition of MDI and PZ was thermally most stable to imply the intrinsic high thermal stability of urea-derivatives of PZ. The higher thermal stability of **8a** and **8b** than **6a** can be attributable to the incorporation of PZ-derived urea function.

CONCLUSIONS

A bifunctional *N*-glucoside **4** was readily prepared from 1,6-hexamethylene diamine by treatment with D-glucose and was employed as a new diamine-type monomer with glucose-derived moieties bearing unprotected hydroxyl groups. The difference in intrinsic nucleophilicity between amino group and hydroxyl group permitted the selective reaction of the former with diisocyanate to give the corresponding polyureas with endowing the side chains with the glucose-derived structure bearing plural hydroxyl groups. The present work has proven the feasibility of our concept "utilization of *N*-glycosylation as a method for facile modification of various amines into the corresponding amine-type monomers." Further exploitation of the present methodology to development of unique monosaccharide-derived polymers will be continued.

REFERENCES AND NOTES

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