

SHORT COMMUNICATIONS

Synthesis of New Hydroxy-bearing Polyurethanes: Polyaddition of D-Glucose-derived Diols with Diisocyanates

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In the past 20th century many kinds of polymeric materials had been produced for our life, from fossil resources such as coal and petroleum, which were important storage carbon resources on the earth. In the 21st century the development of the macromolecular synthesis from the renewable carbon resources and their circulation system is essential for modern human life.¹

Thus naturally occurring polymers and their repeating units, such as saccharides, amino acids and so on, have been frequently adopted as renewable starting blocks for biodegradable and/or biomedical polymeric materials.^{2–25} In our previous articles, we had already reported the macromolecular syntheses from D-glucose(**1**)-derived diols such as D-glucaro-1,4:6,3-dilactone (**2**), methyl D-glucufuranosidurono-6,3-lactone, and 1,4:3,6-dianhydro-D-glucitol (**3**) (as shown in Scheme 1), and from another aldose derivative, for example D-mannaro-1,4:6,3-dilactone, and found that the polyurethanes containing the dilactone or lactone rings could be hydrolyzed in a neutral phosphate buffer solution to the corresponding saccharide derivatives, diamines, and carbon dioxide at 27 °C more quickly than polyurethanes containing no lactone ring.^{20–22}

In the present work, another D-glucose-derived diols such as methyl 4,6-*O*-benzylidene- α -D-glucopyranoside (**4**) and 1,2:5,6-di-*O*-isopropylidene-D-glucitol (**5**) were prepared through the selective protection of hydroxy groups in D-glucose derivatives with benzylidene or isopropylidene groups, respectively, whereas the D-glucose-derived diols **2** and **3** were prepared by the intramolecular cyclization of D-glucaric acid and D-glucitol, respectively. Then these D-glucose-derived diols **4** and **5** were applied to the macromolecular syntheses of novel polyurethanes (**7** and **8**) by their polyaddition with hexamethylene diisocyanate

(**6a**) and methyl (*S*)-2,6-diisocyanatohexanoate (lysine diisocyanate, **6b**) as shown in Scheme 2. In addition, novel hydroxy-bearing polyurethanes (**9** and **10**) were synthesized by the subsequent deprotection in trifluoroacetic acid aqueous solution.

EXPERIMENTAL

Reagents

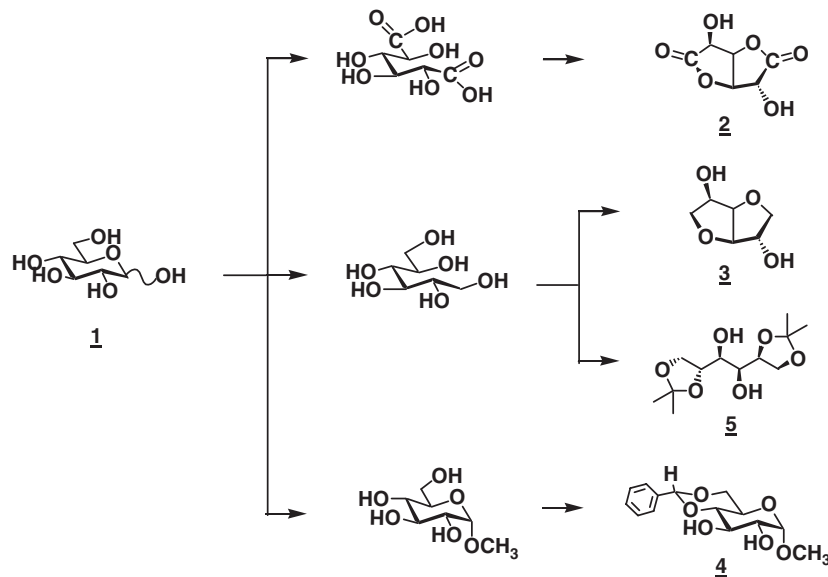
Hexamethylene diisocyanate (**6a**) was purchased from Tokyo Kasei Co. (Japan) and methyl (*S*)-2,6-diisocyanatohexanoate (**6b**) prepared from L-lysine was provided from Kyowa Hakko Kogyo Co. Ltd. (Japan). They were purified by the distillation under reduced pressure just before use. *N,N*-Dimethylformamide (DMF) and dimethyl sulfoxide (Me₂SO) were dried over calcium hydride and distilled under reduced pressure. D-Glucose (**1**), D-glucitol, dibutyltin dilaurate and other reagents were used without purification.

Methyl 4,6-*O*-Benzylidene- α -D-glucopyranoside (**4**)

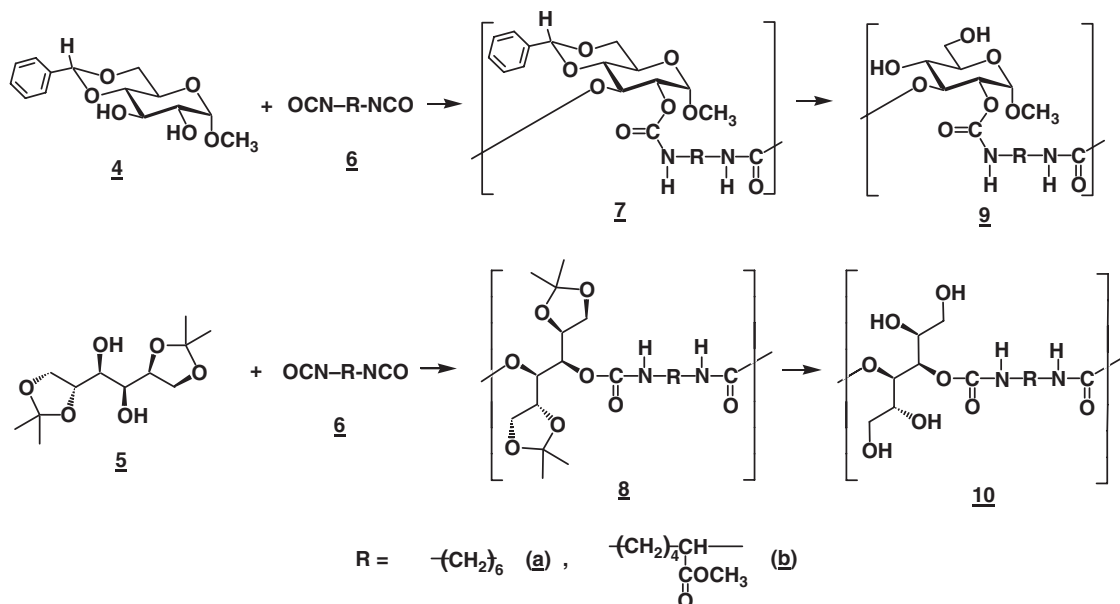
In a 300-mL round-bottomed flask, a mixture of **1** (50.5 g) and 2.5% hydrochloric acid methanol solution (134 mL) was refluxed for 5.5 h, until **1** was completely consumed, which was confirmed by the TLC analysis. Then the solution was cooled down, and the resulting crude crystals of methyl α -D-glucopyranoside were collected and purified by the recrystallization from methanol: yield, 16.5 g (30%); mp, 166 °C (lit, 166 °C).²⁶

According to the method described by M.E. Evans,²⁷ methyl α -D-glucopyranoside (10.0 g), benzaldehyde dimethyl acetal (7.8 g), and *p*-toluenesulfonic acid monohydrate (25 mg) were dissolved in 40 mL of DMF in a 300-mL flask equipped with an evaporator. The mixture was refluxed at 60 °C under reduced pressure for 1 h during the stirring of the flask, and

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Scheme 1.



Scheme 2.

then DMF was distilled out at 100 °C to give a colorless residue. Sodium hydrogen carbonate (1.0 g) in 50 mL of deionized water was added to the flask, and the mixture was heated at 100 °C in order to disperse the residual solid in the solution. After cooling at room temperature, the insoluble part was collected, washed with deionized water, and dried *in vacuo*, which was recrystallized from 1-propanol to isolate **4** as colorless powder.

Yield, 11.4 g (79%); mp, 171 °C (lit, 167.5–168.5 °C).²⁷ ¹H NMR [Me₂SO-*d*₆, δ, ppm]: 7.43 and 7.34 (m, 3H + 2H, aromatic protons), 5.56 (s, 1H, –O–CH–O– in a benzylidene group), 5.2 and 4.9 (broad singlet, 1H + 1H, –OH), 4.63 (d, ¹CH in a py-

ranose ring), 4.15 (dd, 1H, ⁵CH in a pyranose ring), 3.70, 3.58, 3.35 (m, 1H + 2H + 2H, ²CH + ³CH + ⁴CH + ⁶CH₂ in a pyranose ring), 3.32 (s, 3H, –OCH₃).

1,2:5,6-Di-O-isopropylidene-D-glucitol (**5**)

By reference to the method described by Chittenden,^{28,29} D-glucitol (25 g) was suspended with vigorous stirring in 1,2-dimethoxyethane (60 mL) containing tin(II) dichloride (25 mg). Then 2,2-dimethoxypropane (40 mL) was added to the suspension, and it was refluxed with continuous stirring for 1 h, until an almost clear solution was obtained. The solution was cooled, treated with a few drops of pyridine, and concentrated under reduced pressure. The residue

was found to contain at least six components by the TLC analysis (*R_f*, 0.73, 0.46, 0.22, 0.19, 0.13, 0.10, 0.00). Therefore the residue was chromatographed on silica gel by using ethyl acetate–*n*-hexane mixture (1:1 v/v) as an eluent. The eluate containing the third component (*R_f*, 0.22) was collected and concentrated under pressure. The resulting crude crystals were purified by the recrystallization from di-*n*-butyl ether to give colorless needle crystals of **5**.

Yield, 3.6 g (10%); mp, 94–96 °C (lit. 95–95.5 °C).³⁰ ¹H NMR [Me₂SO-*d*₆, δ, ppm]: 4.74 and 4.68 (d, 1H × 2, –OH), 4.09 and 4.03 (t, 1H × 2, –CH– in five-membered rings), 3.94, 3.83, and 3.54 (1H+2H+1H, –CH₂– in five-membered rings), 3.47 and 3.20 (t, –CH–OH), 1.32, 1.30, 1.27, and 1.25 (s, 3H × 4, –CH₃). ¹³C NMR [Me₂SO-*d*₆, δ, ppm]: 108.1 and 108.0 (quaternary carbon in isopropylidene groups), 77.5 and 75.2 (methine carbons in five-membered rings), 71.5 and 71.0 (–CH–OH), 66.1 and 65.4 (methylene carbons in five-membered rings), 26.8, 26.7, 25.6, 25.4 (–CH₃).

Polyaddition of D-Glucose-derived Diol (5) with Hexamethylene Diisocyanate (6a)

In a dry box filled with dry nitrogen, equimolar amounts of **5** (2.62 g, 9.93 mmol) and **6a** (1.67 g, 9.93 mmol) were strictly weighed and dissolved in 6.2 mL of DMF in a glass ampoule, and di-*n*-butyltin dilaurate (91 mg) was added to the solution drop by drop with stirring at room temperature. Then the ampoule was kept in a bath controlled at 50 °C for 24 h. After quenching with a small amount of methanol for 24 h, the reaction mixture was poured into 100–200 mL of diethyl ether. The resulting polymer was collected, washed with deionized water repeatedly, and dried *in vacuo*. Yield of **8a**, 3.73 g (87%).

Deprotection of Polyurethanes

Polyurethane (**7a**, 513 mg) prepared from **4** and **6a** was added into a mixture of trifluoroacetic acid (50 mL) with deionized water (25 mL), and the mixture was stirred vigorously at 15 °C for 5 h. Then the solvent was distilled out under reduced pressure, and the residue was powdered in deionized water and dried *in vacuo*. Yield of **9a**, 367 mg (89%).

Measurements

Polymeric structures were examined by ¹H NMR, ¹³C NMR, and their two-dimensional analysis with a JEOL EX-270 Fourier transform high-resolution nuclear magnetic resonance spectrometer. Deuteriodimethyl sulfoxide and tetramethylsilane (TMS) were used as a solvent and an internal standard, respectively. The average molecular weight of the polyurethanes was determined by a TOSOH Model HLC-8120 high-

performance liquid chromatograph (column, TOSOH TSK-gel GMHXL, φ7.8 × 600 mm or Super HM-M, φ6.0 × 300 mm; solvent, Me₂SO; rate, 0.15 mL/min). The fractionated pullulans with different molecular weight were provided as standards. Thermal stability was examined with a Rigaku Model TG8120 thermogravimetric analyzer from 30 to 500 °C at a heating rate of 10 °C/min under dry nitrogen atmosphere. The degradation point was defined as a temperature at which 10 wt% of the polymer was reduced. The differential scanning calorimetry (DSC) was carried out on a Rigaku Model DSC8230L instrument under dry nitrogen atmosphere at a heating rate of 10 °C/min, after keeping at near decomposition temperature for 15 min and cooling down to room temperature at a rate of 10 °C/min.

RESULTS AND DISCUSSION

Monomer Synthesis

The selective protection of hydroxy groups at the 4th and 6th positions in methyl α-D-glucopyranoside proceeded in high yield according to the literature:²⁷ yield of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**4**), 79%. However, the synthesis of 1,2:5,6-di-*O*-isopropylidene-D-glucitol (**5**) from D-glucitol was more troublesome, because the reaction of D-glucitol with excess of 2,2-dimethoxypropane proceeded step by step to give the corresponding mono-, di-, and triisopropylidene derivatives. After reflux for 1 h, **5** was isolated by the preparative chromatography of silica gel from the reaction mixture containing more than six components. Therefore the yield of **5** was relatively low (10%). After the purification, the monomers were dried *in vacuo* in the presence of phosphorous pentoxide before use.

Polyaddition of D-Glucose-derived Diols (4 and 5) with Diisocyanates (6)

As described in the experimental section, equimolar amounts of D-glucose-derived diols (**4** or **5**) with hexamethylene diisocyanate (**6a**) or methyl (*S*)-2,6-diisocyanatohexanoate (**6b**) were allowed to react by using di-*n*-butyltin dilaurate as a catalyst at 25 or 50 °C. The polyaddition proceeded smoothly and the reaction mixture became viscous.

The yield of the resulting colorless polymers was almost quantitative except in the case of the polyaddition of **5** and **6b** accompanied with mechanical loss, as shown in Table I.

The average molecular weights of the polymers obtained from **5** and **6** were estimated by the gel permeation chromatography (GPC) in dimethyl sulfoxide to be higher than those obtained from **4** and **6**. The higher temperature (50 °C) is thought to be preferential for

Table I. Polyaddition of D-glucose-derived diols (**4** and **5**) with diisocyanates^a

Diol	Diisocyanate		DMF (mL)	Temp. (°C)	Time (h)	Polymer yield		$M_n \times 10^{-3b}$
	g (mmol)	g (mmol)				%		
4	0.92 (3.26)	6a 0.55 (3.26)	2.5	25	24	7a	90	4.8
4	0.94 (3.33)	6a 0.56 (3.33)	2.5	25	72	7a	91	9.0
4	1.02 (3.62)	6b 0.76 (3.60)	2.5	25	24	7b	100	3.1
4	0.95 (3.36)	6b 0.71 (3.36)	2.5	25	72	7b	99	5.2
5	2.60 (9.93)	6a 1.67 (9.93)	6.2	50	24	8a	87	13.2
5	1.58 (6.00)	6b 1.27 (6.00)	6.2	50	24	8b	32 ^c	12.2

^aMole ratio of diol to diisocyanate, 1.00; catalyst, di-*n*-butyltin dilaurate, 1 mol %/monomer. ^bBy GPC in Me₂SO (standard, fractionated pullulan). ^cA portion of polyurethane was lost mechanically.

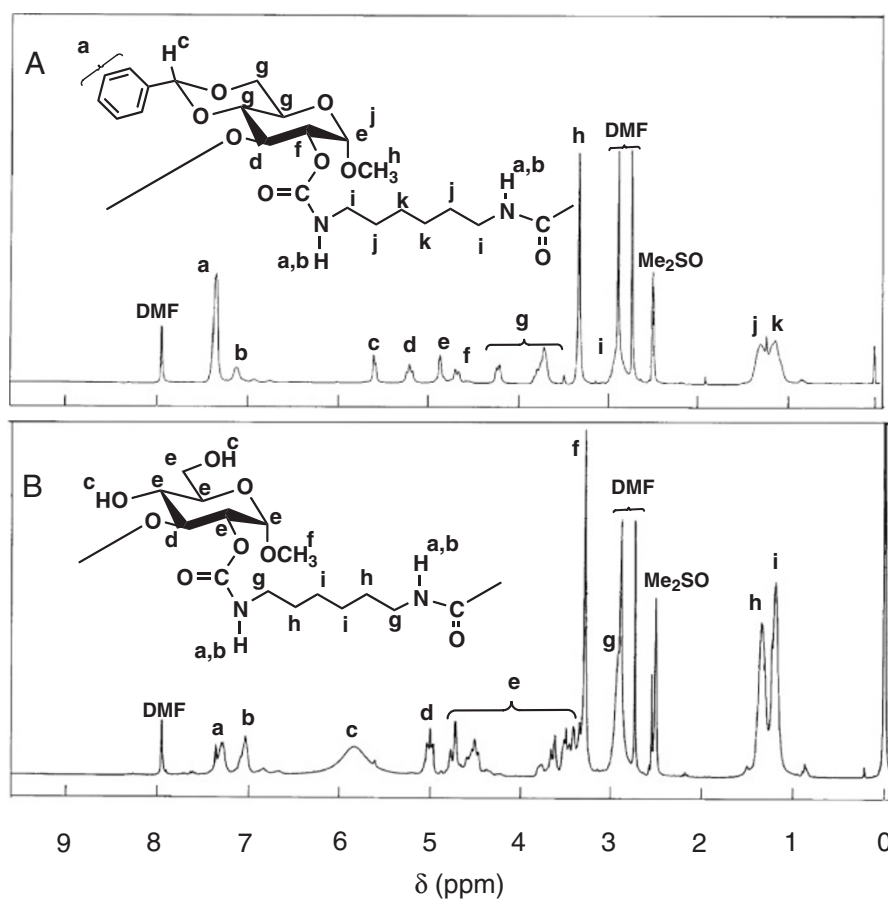


Figure 1. ¹H NMR spectra of polyurethanes prepared from methyl 4,6-*O*-benzylidene-D-glucopyranoside (**4**) and hexamethylene diisocyanate (**6a**): (a) before deprotection (**7a**); (b) after deprotection (**8a**) (5% Me₂SO-*d*₆ solution, TMS, room temperature, 270 MHz).

the present polyaddition. A similar behavior has been observed in the polyaddition of another saccharide-derived diols, 1,2:5,6-di-*O*-isopropylidene-D-mannitol, and 1,2-*O*-isopropylidene-D,L-erythritol with diisocyanates in our unpublished data.³¹

Another reason may be caused by the difference of the steric hindrance in the D-glucose-derived diols. The hydroxy groups in both diols **4** and **5** are surrounded by bulky groups, which may slow down the polyaddition rate. In addition, the hydroxy groups in **4** are located in the rigid pyranose ring, of which the conformational transition may be disturbed by

the benzylidene group. Therefore the hydroxy groups in **5** may rotate more freely than **4**.

The main signals in the ¹H NMR spectrum of the polymer obtained from **4** and **6a** are assigned to the protons in the expected polyurethane structure (**7a**) as shown in Figure 1(A), although it is contaminated with DMF.

Deprotection of Polyurethanes

The resulting polyurethanes (**7a**, **7b**, **8a**, and **8b**) prepared from diols (**4** and **5**) and diisocyanates (**6a** and **6b**) respectively were stirred in a mixture of

Table II. Deprotection of polyurethanes (**7** and **8**) prepared from D-glucose-derived diols (**4** and **5**) and diisocyanates (**6**)^a

	Polyurethane		Temp. (°C)	Recovered polymer yield		$M_n \times 10^{-3b}$
	$M_n \times 10^{-3}$	mg			%	
7a	9.0	513	15	9a	89	7.1
7b	4.6	597	15	9b	90	14.4
8a	13.2	500	20	10a	86	3.2
8b	12.2	250	20	10b	68	6.8

^aA mixture of trifluoroacetic acid with water (volume ratio 2:1), 75 mL; time, 5 h. ^bBy GPC in Me₂SO (standard, fractionated pullulan).

trifluoroacetic acid and deionized water (2:1 v/v) at 15 °C or 20 °C. During the stirring for 5 h, the suspension solution became more transparent to give a homogeneous solution. After the removal of the solvents, the residual syrup from **7** and **8** was powdered in deionized water or ethyl acetate, respectively, and dried *in vacuo* (see Table II).

The ¹H NMR spectrum in Figure 1(B) indicated that the benzylidene groups in the original polyurethane (**7a**) completely disappeared and that new polyurethanes (**9a**) bearing two hydroxy groups in the pyranose ring was obtained quantitatively. The isopropylidene groups in the polyurethanes (**8**) were also removed in a similar condition to give different types of polyurethanes (**10**) having four hydroxy groups in each repeating unit.

Solubility and Thermal Property of the Polyurethanes

The solubility of the polyurethanes synthesized from diols **4** and **5** (**7** and **8**) in different organic solvents was examined and summarized in Tables III and IV, respectively. Both polyurethanes were soluble in aprotic polar solvents such as DMF, *N,N*-dimethylacetamide, and dimethyl sulfoxide, but insoluble in water, diethyl ether, and *n*-hexane. The solubility of the polyurethanes prepared from methyl (*S*)-2,6-diisocyanatohexanoate (**7b** and **8b**) was found to be higher than that of the polyurethanes prepared from hexamethylene diisocyanate (**7a** and **8a**), respectively.

On the other hand, the solubility of the polyurethanes having hydroxy groups in each repeating unit (**9** and **10**) was lower than that of the original polyurethanes (**7** and **8**), respectively, mainly in non-polar solvents. Another noteworthy point is that the polyurethanes (**10**) with four hydroxy groups in each repeating units were dissolved even in water, but the polyurethanes (**9**) with two hydroxy groups in the corresponding units were not.

All of the polyurethanes obtained in the present work were heated at a constant rate and the weight loss was monitored as shown in Figures 2 and 3.

The degradation temperature was defined as a tem-

Table III. Properties of polyurethanes prepared from methyl 4,6-*O*-benzylidene- α -D-glucopyranoside (**4**)

	Polyurethanes			
	7a	7b	9a	9b
Solubility ^a				
Water	I	I	I	I
Me ₂ SO	S	S	S	S
DMF	S	S	S	S
Methanol	I	s	S	S
Ethanol	I	I	s	s
Acetone	S	S	I	I
Tetrahydrofuran	S	S	S	S
Ethyl acetate	S	S	I	I
Chloroform	S	S	I	I
Diethyl ether	I	I	I	I
<i>n</i> -Hexane	I	I	I	I
Thermal property				
Degradation temperature, ^b °C	280	282	202	195

^a1 g/100 mL; S, soluble at room temperature; s, soluble at 40 °C; I, insoluble. ^bDefined as the temperature at which 10 wt % of the polyurethane was lost.

Table IV. Properties of polyurethanes prepared from 1,2:5,6-di-*O*-isopropylidene-D-glucitol (**5**)

	Polyurethanes			
	8a	8b	10a	10b
Solubility ^a				
Water	I	I	S	S
Me ₂ SO	S	S	S	S
DMF	S	S	S	S
Methanol	S	S	S	S
Ethanol	I	I	S	I
Acetone	I	S	I	I
Tetrahydrofuran	S	S	I	i
Ethyl acetate	I	S	I	I
Chloroform	S	S	I	I
Diethyl ether	I	I	I	I
<i>n</i> -Hexane	I	I	I	I
Thermal property				
Degradation temperature, ^b °C	258	257	216	211

^a1 g/100 mL; S, soluble at room temperature; s, soluble at 40 °C; I, insoluble. ^bDefined as the temperature at which 10 wt % of polymer was lost.

perature at which 10 wt % of the samples were reduced, and summarized in Tables III and IV. The degradation temperature of the protected polyurethanes (**7** and **8**) was relatively high (about 280 °C), regardless of diisocyanates provided for the polyaddition, whereas the deprotected polyurethanes (**9** and **10**) began to degrade at lower temperature than in the cases of the protected ones. Such a thermal degradation of

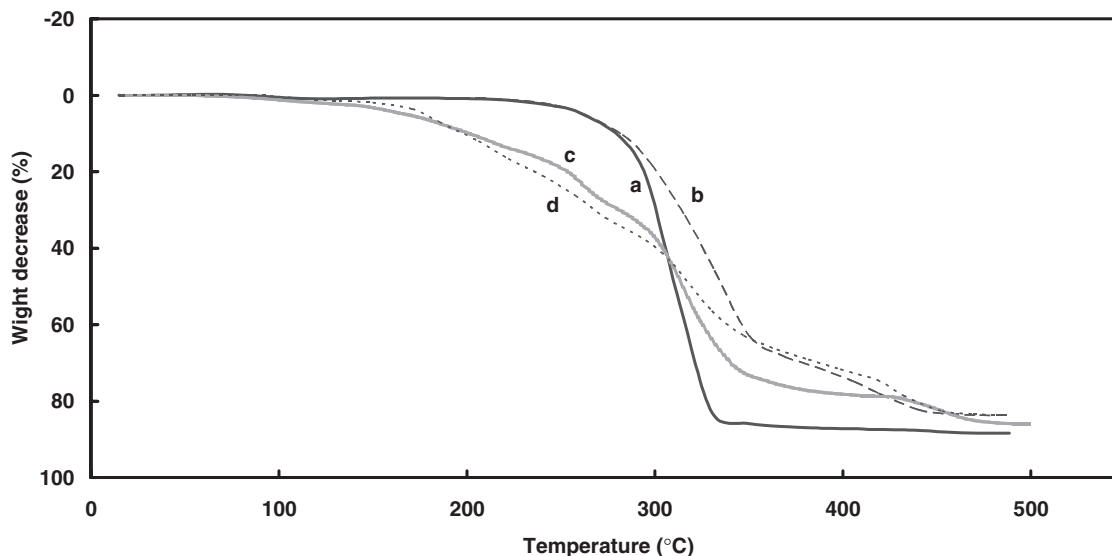


Figure 2. Thermogravimetric curves for several polyurethanes prepared from methyl 4,6-*O*-benzylidene- α -D-glucopyranoside (**4**) and diisocyanates (heating rate, 10 °C/min). (a) Polyurethane **7a** (prepared from **4** and hexamethylene diisocyanate (**6a**)); (b) polyurethane **7b** (prepared from **4** and methyl (*S*)-2,6-diisocyanatohexanoate (**6b**)); (c) polyurethane **9a** (isopropylidene group of **7a** was deprotected); (d) **9b** (isopropylidene group of **7b** was deprotected).

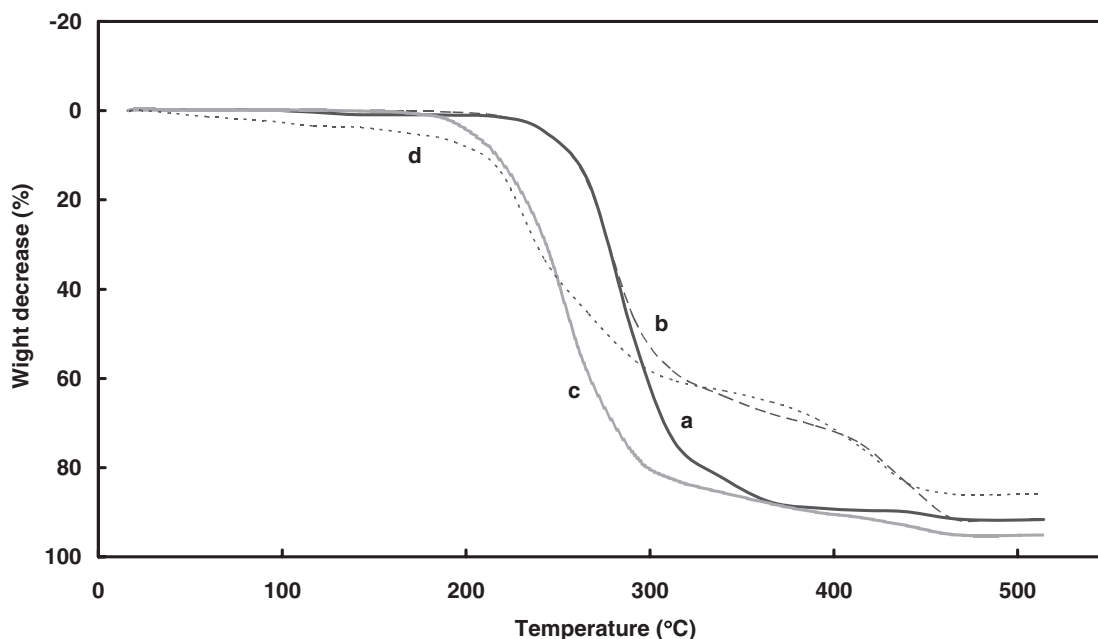


Figure 3. Thermogravimetric curves for several polyurethanes prepared from 1,2:5,6-di-*O*-isopropylidene-D-glucitol (**5**) and diisocyanates (heating rate, 10 °C/min): (a) Polyurethane **8a**; (b) polyurethane **8b**; (c) polyurethane **10a**; (d) polyurethane **10b**.

the hydroxy-bearing polyurethanes at relatively low temperature may be attributed to the degradation associated with the sugar moieties, and the degradation at about 280 °C is due to the degradation of the urethane bonds in the main chains.

On the differential scanning calorimetric analysis of all the resulting polyurethanes, no clear endothermic peak due to their melt or recrystallization was found below the degradation temperature on the repeated heating or cooling process. This fact indicates that

the polyurethanes prepared in the represent work are almost amorphous. The influence of hydroxy groups on the hydrolyzability of the polyurethanes will be investigated and reported near future.

In summary, new polyurethanes (**9** and **10**) bearing two and four hydroxy groups in the repeating units were obtained almost quantitatively by the polyaddition of the D-glucose-derived diols, methyl 4,6-*O*-benzylidene- α -D-glucopyranoside (**4**) and 1,2:5,6-di-*O*-isopropylidene-D-glucitol (**5**), with diisocyanates (**6a**

and **6b**) and the following deprotection. The thermal stability of polyurethanes bearing hydroxy groups (**9** and **10**) was found to be much lower than that of the corresponding protected polyurethanes (**7** and **8**).

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