Anionic ring-opening polymerization of a five-membered cyclic urethane derived from D-glucosamine

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ABSTRACT: The anionic ring-opening polymerization of a five-membered cyclic urethane, 2-amino-4,6-*O*-benzylidene-2-*N*,3-*O*-carbonyl-2-deoxy-α,D-glucopyranoside (MBUG), which was prepared from naturally abundant D-glucosamine, was examined. Potassium *tert*-butoxide (t-BuOK) was the most effective initiator among the evaluated bases and produced polyurethane with the Mn of 7800 without any elimination of CO_2. The equimolar reaction of MBUG and t-BuOK in the presence of CH_3I produced *N*-methylated MBUG and suggested that the initiation reaction involves proton abstraction from the NH group. This *N*-methylated compound did not undergo the polymerization. Therefore, the mechanism of propagation in the ROP of MBUG should involve the proton abstraction and nucleophilic substitution of the resulting amide anion. © 2019 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**

KEYWORDS: anionic polymerization; ring-opening polymerization; cyclic urethane; polyurethane; glucosamine

INTRODUCTION Polyurethanes are generally prepared by the polyaddition reaction of diisocyanates with diols. Höcker and his co-workers proposed that the ring-opening polymerizations (ROPs) of cyclic urethanes are useful alternatives for the polyurethane synthesis.[1–3] This type of polymerization has the potential to copolymerize with the other cyclic monomers such as lactones, cyclic carbonates, lactams, and so on. However, the polymerizability of the cyclic urethanes usually depends on their ring size and initiators. Hall and Schneider mentioned that the five-membered cyclic urethane decomposes upon heating in the presence of sodium or sodium hydride, although six-membered cyclic urethanes are ROP polymerizable.[4] The cationic polymerizations of six-[2,3] or seven-membered[1] cyclic urethanes produce linear polyurethanes, while there are no reports about polyurethane syntheses by the ROP of five-membered cyclic urethane.

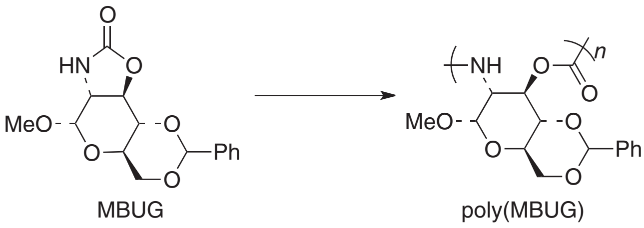
Similarly, the five-membered cyclic carbonate is believed to be an unsuitable monomer to produce polycarbonates. The ROP of such a cyclic carbonate proceeds only at a relatively higher temperature and causes elimination of a significant amount of CO_2 to give carbonate/ether copolymers.[5–10] However, our investigation about the anionic ROP of a five-membered cyclic carbonates, methyl 4,6-*O*-benzylidene-2,3-*O*-carbonyl-α,D-glucopyranoside (MBCG),[2,3] its alternatives derived from α,D-galactopyranoside[11] and *trans*-cyclohexane-1,2-diyl carobonate,[12] showed that the polymerization proceeded at 60 °C without any elimination of CO_2 and produced a polycarbonate containing no polyether repeating units, although the presence of backbiting reaction during the ROP was noted.[13] Wooley and co-workers later reported that the polymerization of MBCG should be controllable using organocatalyst systems.[14] On the other hand, such an ROP did not occurred with an MBCG isomer derived from α,D-mannnopyranoside[11] and *cis*-cyclohexane-1,2-diyl carbonate.[12] Thus, the unusual high polymerizability of MBCG may be caused by the ring-strain of MBCG, whose carbonate ring connects to a cyclic structure in a *trans* fashion.

Crich and Vinod reported the synthesis of 2-amino-4,6-*O*-benzylidene-2-*N*,3-*O*-carbonyl-2-deoxy-α,D-glucopyranoside (MBUG) from the naturally abundant D-glucosamine.[15] MBUG can be regarded as a urethane analog of MBCG. Considering the results of the polymerization of MBCG, MBUG seems to also have the potential to polymerize in spite of the thermodynamically unfavorable nature of the five-membered cyclic urethanes (Scheme 1). In this study, we examined the anionic polymerizations of MBUG. We will also report the structure of the reaction products and the reaction mechanisms.

EXPERIMENTAL

Measurements

The infrared (IR) spectra were recorded using a HORIBA FT-210 spectrometer. The ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ by a JEOL JNM-ECX 400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer at room temperature. The chemical shift values were in ppm downfield from tetramethylsilane (0.0 ppm) and $CDCl_3$ (77.0 ppm) used as the internal standards for the ^1H and ^{13}C measurements,



SCHEME 1 ROP of MBUG.

respectively. The assignments were made by using ^{1}H-^{1}H COSY and ^{13}C-^{1}H HETCOR spectra. The number-average (*M*n) and weight-average (*M*w) molecular weights were estimated by size-exclusion chromatography (SEC) using a Tosoh DP-8020 GPC and polystyrene gel columns (Tosoh TSK gels G2500H, G3000H, G4000H, and GMH) in THF using a calibration curve of polystyrene standards. The thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC) results were recorded by a Seiko SSC/5200 (DSC 220) instrument at the heating/cooling rate of 10 °C/min under a nitrogen atmosphere.

Materials

MBUG was prepared from D-glucosamine hydrochloride according to the procedure reported by Critch and Vinod.[15] Methyl 4,6-*O*-benzylidene-α,D-glucopyranoside (**4**)[16] and methyl 4,6-*O*-benzylidene-2,3-bis-*O*-ethoxycarbonyl-α,D-glucopyranoside (**5**)[17] were prepared by the reported procedures. *N,N*-Dimethylformamide (DMF, Kanto Chemicals) was distilled from CaH_2 under reduced pressure. Potassium *tert*-butoxide (*t*-BuOK, 1.0 M in THF; Sigma-Aldrich), lithium *tert*-butoxide (*t*-BuOLi, 1.0 M in THF; Sigma-Aldrich), *n*-butyllithium, (1.6 M solution in *n*-hexane, Kanto Chemicals), *t*-butyllithium (1.6 M solution in *n*-pentane, Kanto chemicals), and lithium diisopropylamide (1.0 M solution in n-hexane/THF, Kanto Chemicals) were purchased and used as received. 1,9-Diazabicyclo[4.3.0]undec-7-ene (DBU) was obtained from Kanto Chemicals and distilled from CaH_2 under reduced pressure. All other chemicals were commercially available and used without further purification.

Polymerization of MBUG

A typical procedure was as follows: In a test tube equipped with a three-way stopcock and filled with nitrogen, MBUG (0.41 g, 1.3 mmol) was dissolved in DMF (0.8 ml, 3.0 mol·l^{-1}). The solution was cooled to 0 °C, and then an initiator, *t*-BuOK (1.0 M solution in THF, 0.10 ml, 0.10 mmol), was added via a syringe. The solution was stirred at this temperature for 12 h. Acetic acid (12 μl) was added to quench the reaction, and the solution was poured into an ice-cold methanol (50 ml). The white precipitate was collected by filtration, reprecipitated from $CHCl_3$-methanol and dried *in vacuo* at room temperature. Yield 0.30 g (74%). Mn = 7800 (SEC).

Methyl 2-(*N*-Methylamino)-4,6-*O*-Benzylidene-2-*N*,3-*O*-Carbonyl-2-Deoxy-α,D-Glucopyranoside (6)

To a solution of MBUG (1.0 g, 3.4 mmol) in THF (50 ml), CH_3I (2.0 mol, 33 mmol) was added at 0 °C under a nitrogen atmosphere. A 1.0 M solution of *t*-BuOK in THF (3.4 ml, 3.4 mmol) was added and the solution was stirred for 20 min. Water (73 μl) was added to quench the reaction and volatiles were removed under reduced pressure. The aqueous residue was extracted by $CHCl_3$. The organic layer was washed with water, dried over $MgSO_4$, and evaporated to dryness. The residue was purified on a silica-gel column with $CHCl_3$/EtOAc (6/1, v/v) to give a white solid. Yield 0.40 g (36%). ^{1}H-NMR (in $CDCl_3$, 400 MHz): δ(ppm) = 7.52–7.36 (m, 5H, Ph), 5.61 (s, 1H, C*H*Ph), 5.00 (d, $J_{1\text{-}2}$ = 2.7 Hz, 1H, H-1), 4.64 (dd, $J_{3\text{-}2}$ = 11.3 Hz, $J_{3\text{-}4}$ = 10.0 Hz, 1H, H-3), 4.30 (dd, ^2J = 9.3 Hz, $J_{6eq\text{-}5}$ = 3.9 Hz, 1H, H-6$_{eq}$), 4.04 (dd, $J_{4\text{-}3}$ = 10.0 Hz, $J_{4\text{-}5}$ = 8.2 Hz, 1H, H-4), 3.90–3.85 (m, 2H, H-5 and H-6$_{ax}$), 3.52 (s, 3H, OC*H*$_3$) 3.43 (dd, $J_{2\text{-}1}$ = 2.7 Hz, $J_{2\text{-}3}$ = 11.3 Hz, 1H, H-2) 2.85 (s, 3H, N-C*H*$_3$). ^{13}C-NMR (in $CDCl_3$, 100 MHz): δ (ppm) = 158.9 (C═O), 136.7, 129.3, 128.4, 126.2 (Ar), 101.5 (PhCH), 97.2 (C-1), 80.2 (C-4), 73.6 (C-3), 68.7 (C-6), 65.8 (C-5), 63.8 (C-2), 55.9 (OCH_3), 30.3 (N-*C*H$_3$). $[\alpha]_D^{27}$ = +68.7° (*c* 1.0, $CHCl_3$).

Methyl 4,6-*O*-Benzylidene-2-(Methoxycarbonylamino)-3-*O*-(*N*-Propylcarbamoyl)- 2-Deoxy-α,D-Glucopyranoside (3)

To a solution of methyl 2-amino-4,6-*O*-benzylidene-3-*O*-(*N*-propylcarbamoyl)-2-deoxy-α,D-glucopyranoside[15] (1.0 g, 3.0 mmol) in THF (20 ml), a mixture of n-propylisocyanate (0.30 g, 3.5 mmol) and dibutyltin dilaurate (2.7 g, 4.3 mmol) was added. The resulting solution was stirred at 50 °C for 24 h and then concentrated under reduced pressure. The residue was dissolved in ethyl acetate, washed with water, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give a brown solid, which was purified on a silica gel column with $CHCl_3$/EtOAc = 3/1 (v/v). The resulting white solid was recrystallized from $CHCl_3$/*n*-hexane. Yield 0.45 g (36%). ^{1}H-NMR(in $CDCl_3$, 400 MHz): δ(ppm) = 7.46–7.25 (m, 5H, Ph), 5.50 (s, 1H, C*H*Ph), 5.30 (d, $J_{NH\text{-}2}$ = 9.6 Hz, 1H, NH), 5.15 (t, $J_{3\text{-}2}$ = $J_{3\text{-}4}$ = 10.1 Hz, 1H, H-3), 4.85 (t, *J* = 5.0 Hz, 1H, Pr-NH), 4.72 (d, $J_{1\text{-}2}$ = 3.2 Hz, 1H, H-1), 4.25 (dd, $J_{6eq\text{-}5}$ = 4.9 Hz, ^2J = 10.1 Hz, 1H, H-6$_{eq}$), 3.94 (dt, $J_{2\text{-}1}$ = 3.2 Hz, $J_{2\text{-}3}$ = 10.1 Hz, $J_{2\text{-}NH}$ = 9.6 Hz, 1H, H-2), 3.84 (dd, $J_{5\text{-}6eq}$ = 4.6 Hz, $J_{5\text{-}6ax}$ = 9.62 Hz, 1H, H-5) 3.76 (t, $J_{6ax\text{-}5}$ = 9.6 Hz, $J_{6ax\text{-}6eq}$ = 10.1 Hz, 1H, H-6ax), 3.70–3.60 (m, 4H, H-4, COOC*H*$_3$.), 3.37 (s, 3H, OC*H*$_3$), 3.10–2.94 (m, 2H, NHC*H*$_2$), 1.50–1.35 (m, 2H, NHCH$_2$C*H*$_2$), 0.80 (t, *J* = 7.3 Hz, 3H, NHCH$_2$CH$_2$C*H*$_3$). ^{13}C-NMR (in $CDCl_3$, 100 MHz): δ (ppm) = 156.9 (C═O), 156.3 (C═O), 137.1, 129.1, 128.2, 126.4 (Ar), 101.7 (PhCH),

TABLE 1 Anionic ROP of MBUG at 0 °C for 12 h[a]

Runs	Initiator	Yield[b] (%)	Mn[c] × 10^{-3}	Mw/Mn[c]	$[\alpha]_D$[d]
1	*t*-BuLi	60	1.9	1.6	+67
2	*n*-BuLi	45	1.6	1.4	+68
3	LDA	27	1.4	1.3	+70
4	*t*-BuOK	74	7.8	1.2	+42
5	DBU	56	0.4	1.0	+85

[a] $[MBUG]_0$ = 3.0 mol•l^{-1}, $[MBUG]_0/[I]_0$ = 25, solvent: DMF.

[b] Methanol-insoluble fraction.

[c] Estimated by SEC eluted with DMF based on polystyrene calibration.

[d] Measured in DMF at 25–30 °C, *c* = 1.0.

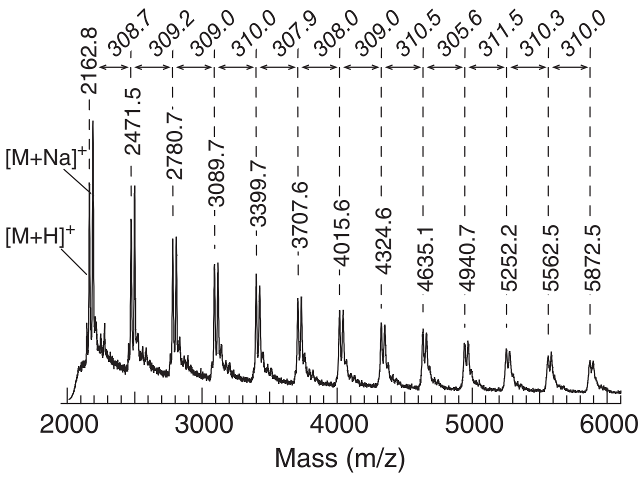


FIGURE 1 MALDI-TOF MS spectrum of poly(MBUG) (Run 4). HABA was used as the matrix.

99.5 (C-1), 79.5 (C-4), 70.6 (C-3), 68.9 (C-6), 62.9 (C-5), 55.4 (C-2), 55.0 (OCH_3), 52.3 ($COOCH_3$), 42.8 ($NHCH_2$), 23.0 ($NHCH_2CH_2$), 11.1 ($NHCH_2CH_2CH_3$). $[\alpha]_D^{27}$ = +20° (*c* 1.0, $CHCl_3$).

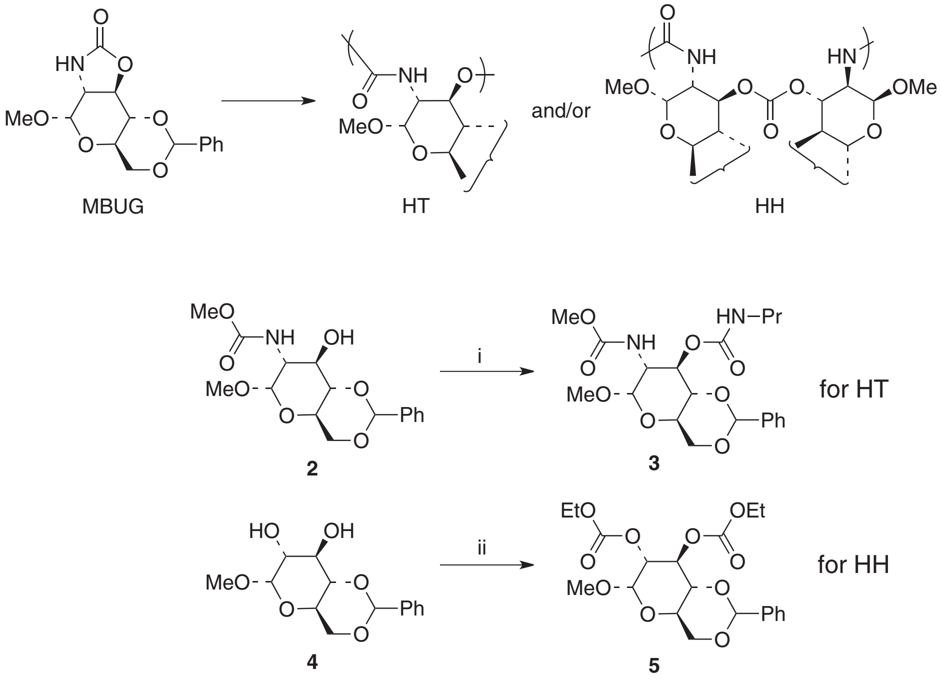
RESULTS AND DISCUSSION

Anionic Polymerization of MBUG

The anionic polymerization of MBUG was carried out at 0 °C for 12 h in DMF. As initiators, *t*-BuLi, *n*-BuLi, LDA, *t*-BuOK, and DBU were used. The polymerization mixture was poured into methanol, and the precipitate was collected by filtration. The results are listed in Table 1. With DBU (Run 5), the methanol-insoluble product was obtained in 56% yield, but this product was only a low-molecular-weight material. When *t*-BuLi, *n*-BuLi, or LDA was used (Runs 1–3), the polymerization proceeded heterogeneously, and the yields and the number averaged molecular weights (Mn's) were low. The polymerization with *t*-BuOK (Run 4) proceeded homogeneously and produced a polymer having relatively large Mn of 7400 in 74% yield. When *t*-BuOLi was used, the polymerization solution become heterogeneous and the yield of the product was also low (*ca.* 30%). So the heterogeneous polymerization in Runs 1–3 might be due to the poor solubility of lithium salt of some intermediate anions. Thus, among the tested initiators, *t*-BuOK was the most suitable for the polymerization of MBUG.

Figure 1 shows MALDI-TOF MS spectra of the polymers obtained with t-BuOK (Run 4). The spectrum shows two sets of peaks. Because the difference of m/z values in one set was almost 22, each peak should be attributed to $[M + H]^+$ and $[M + Na]^+$. The m/z value differed by 308–310 Da intervals between each set. This interval agreed with the molecular weight of MBUG (307.1). If the elimination of CO_2 occurs during the polymerization, the molecular weight of the repeating units should be 263.3. Because such an interval was not observed, the elimination of CO_2 did not occur during the polymerization, and the polymer should have carbonyl groups in a quantitative amount.

For the polymer without any decarbonylation, head-to-tail urethane (HT) and head-to-head carbonate-urea (HH) structures



SCHEME 2 Possible repeating units for poly(MBUG) and syntheses of the corresponding model compounds. Conditions: (i) Pr-NCO, $SnBu_2(lau)_2$, THF, 50 °C, 24 h, (ii) EtOCOCl, pyridine, THF, rt.

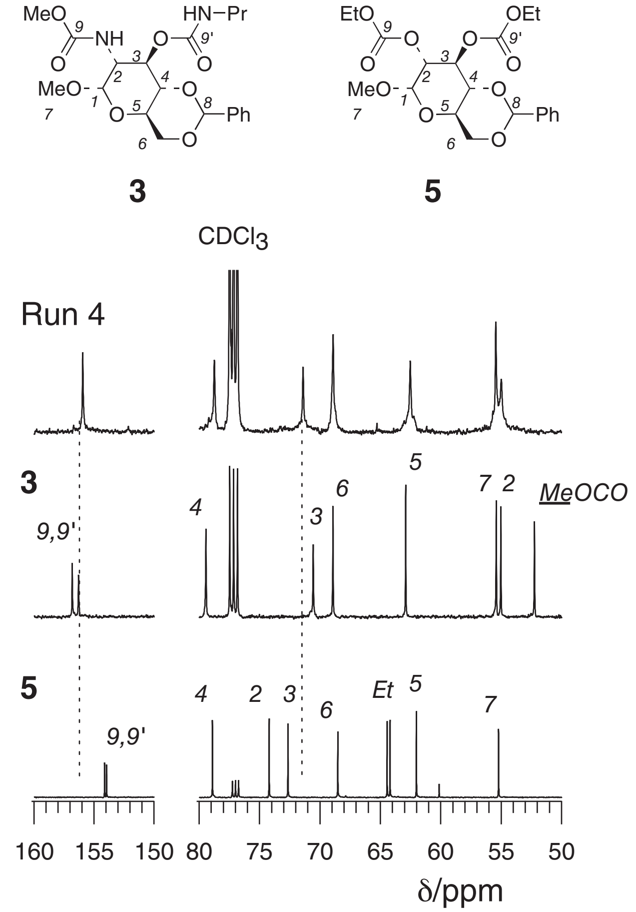


FIGURE 2 ^{13}C NMR spectra of poly(MBUG) (Run 4), and model compounds **3** and **5**, measured in $CDCl_3$ at rt.

might be possible (Scheme 1). In order to further confirm the polymer structure, two model compounds **3** and **5** for the HT and HH units, respectively, were prepared (Scheme 2). The former was prepared from a reaction of methyl 2-methoxycarbonylamino-4,6-*O*-benzylidene-2-deoxy-α,ᴅ-glucopyranoside (**2**), which is an intermediate in the synthesis of MBUG, with *n*-propyl isocyanate in the presence of dibutyltin dilaulate. The latter was previously prepared[17] from the reaction of methyl 4,6-*O*-benzylidene-α,ᴅ-glucopyranoside (**4**) and ethyl chlorocarbonate. Figure 2 shows the ^{13}C NMR spectra of the polymer obtained in Run 4 and the model compounds. Only one carbonyl peak at 155.9 ppm was observed in the spectrum of the poly(MBUG), which corresponded to those of **3** at 156.9 and 156.3 ppm rather than those of **5** at 154.0 and 154.1 ppm. The carbon at the 3-position of poly(MBUG) (71.4 ppm) also agreed with that of **3** (70.6 ppm) rather than that of **5** (72.7 ppm). In addition, the previously reported polycarbonate, poly(MBCG), showed the carbonyl carbon and C-3 at 153.3 and 72.9 ppm, respectively, which could not be observed in the spectrum of poly(MBUG). The poly(MBUG) obtained in Run 4, therefore, should contain no carbonate units, and mainly consists of the head-to-tail urethane repeating units.

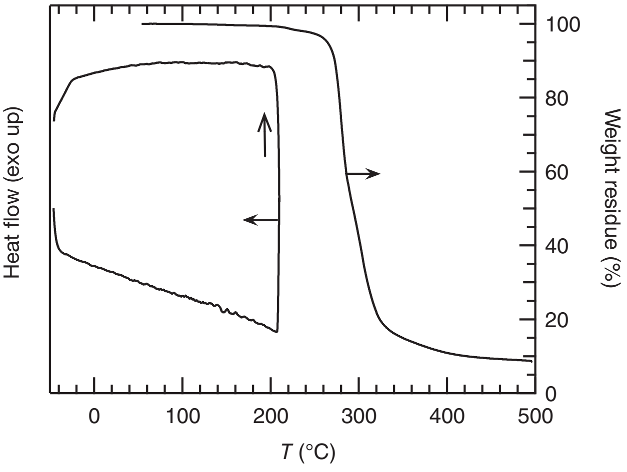


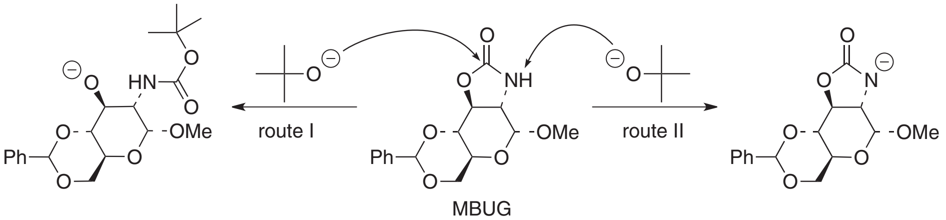
FIGURE 3 DSC trace in the second heating/cooling scan and TGA trace of poly(MBUG) (Run4). Each trace was recorded at $\Delta T = 10\,^{\circ}C\ min^{-1}$.

Table 2 shows the results of the polymerization of MBUG by varying the polymerization conditions such as the temperature and time. For the temperature (Runs 6, 4, 11, 12), the polymerization at 0 °C gave the highest Mn (7800) in the best yield (74%). At the lower temperature (Run 6), the

TABLE 2 Anionic ROP of MBUG with *t*-BuOK[a]

Runs	Temp. (°C)	Time (h)	Yield[b] %	Mn[c] × 10^{-3}	Mw/Mn[c]	$[\alpha]_D$[d]
6	–30	12	60	5.0	1.2	+44
7	0	1	48	3.8	1.1	+45
8	0	3	72	4.9	1.2	+43
9	0	6	75	5.1	1.2	+44
10	0	9	70	5.3	1.2	+41
4	0	12	74	7.8	1.2	+42
11	30	12	33	3.4	1.2	+27
12	60	12	13	2.1	1.2	+33

[a] $[MBUG]_0 = 3.0$ mol•l^{-1}, $[MBUG]_0/[t\text{-}BuOK]_0 = 25$, solvent: DMF.
[b] Methanol-insoluble fraction.
[c] Estimated by SEC eluted with DMF based on polystyrene calibration.
[d] Measured in DMF at 25–30 °C, *c* = 1.0.



SCHEME 3 Possible initiation mechanism for ROP of MBUG.

polymerization was too slow and considerable amounts of the unreacted monomer remained. The higher temperature (Runs 11–12) caused a decrease in both the Mn and polymer yield, which might be the result of polymer decomposition. By varying the polymerization time at 0 °C (Runs 7–10, 4), the Mn and yield increased within 3 h and remained constant around Mn of 5000 and 70% yield. Thus, the polymerization at 0 °C was almost completed within 3 h.

Figure 3 shows the TGA and DSC traces of the resulting poly(MBUG) (Run 4). The 5% weight loss temperature (T_{d5}) was 264 °C. The DSC trace did not show any significant phase and glass transitions within the range of −50 to 210 °C. Thus, poly(MBUG) should be an amorphous polymer with a relatively high heat resistance.

Polymerization Mechanism

For the initiation reaction of anionic polymerization of the cyclic urethanes, the two mechanisms shown in Scheme 3 might be possible. One is a nucleophilic addition-elimination reaction of nucleophiles toward the urethane carbonyl group (route I). Another involves an abstraction of the NH proton (route II), which is generally proposed for the anionic ROPs of lactams. In order to confirm which route the polymerization of MBUG initiates, an equimolar reaction of MBUG with *t*-BuOK was carried out. Figure 4 shows the ^{13}C NMR spectrum of the obtained chromatographically pure product. The product showed no *t*-butyl groups around 30 ppm in the ^{13}C NMR spectrum. If the reaction proceeds according to route I, the product should be the 2-*N*-*t*-butoxycarbonyl compound. The absence of *t*-butyl groups therefore denies route I. In addition, this equimolar reaction between MBUG and t-BuOK was carried out in the presence of 1 equivalent of CH_3I as an anion trapper. This reaction gave the *N*-methyl derivative **6** in 36% yield after purification by column chromatography. This result also suggests that the initiation reaction requires proton abstraction from the NH group to form the amide anion.

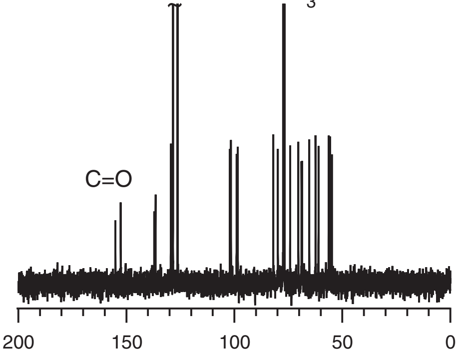
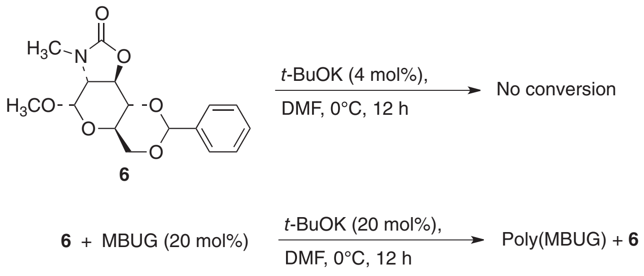


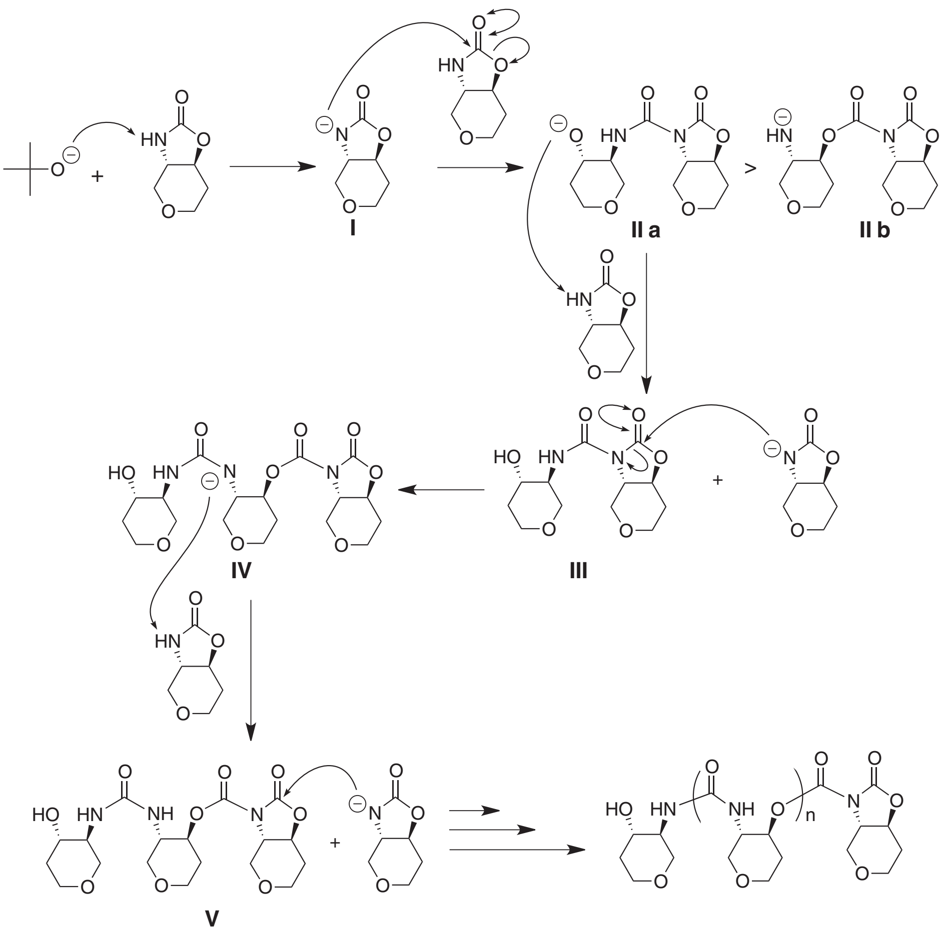
FIGURE 4 ^{13}C NMR spectrum of the product from the equimolar reaction between MBUG and *t*-BuOK.

The same polymerization condition as Run 4 was employed for **6**, but no methanol-insoluble product was obtained, and the unreacted **6** was quantitatively recovered from the reaction mixture. Next, the polymerization of **6** was examined in the presence of 20 mol % *t*-BuOK and MBUG. If the proton abstraction is required only in the initiation reaction, the initiation should occur between *t*-BuOK and MBUG and then the propagation of **6** should proceed. The methanol-insoluble fraction from the resulting mixture, however, consisted only of poly(MBUG), and the unreacted **6** was quantitatively recovered (Scheme 4). These results should indicate that the polymerization of MBUG requires proton abstraction during both the initiation and propagation reactions.

Based on the aforementioned results, the polymerization mechanism of MBUG was considered as shown in Scheme 5. Table 3 lists the p*K*a values of the related compounds in DMSO that appeared in the literature. Because the cyclic urethane (p*K*a = 20.8) could be regarded as a stronger acid than *t*-butanol (p*K*a = 32.2), the initiator, *t*-BuOK, should react with MBUG to form the cyclic amide ion (**I**). The other MBUG undergoes nucleophilic addition by **I** to produce a dimer anion (**II**) in which one MBUG unit retains a cyclic structure and the other has the ring-opened units. In this step, C—O scission (to give **IIa**) and C—N scission (to give **IIb**) might be possible.



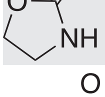
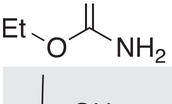
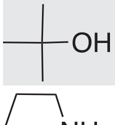
SCHEME 4 Reactions of **6** with t-BuOK in the presence/absence of MBUG



SCHEME 5 Plausible mechanism for the anionic polymerization of MBUG with t-BuOK. The structure of MBUG is partly omitted except for pyranose and the urethane rings.

Because alcohols (p*K*a ~ 32) are stronger acids than amines (p*K*a ~ 44), the alkoxide anion **IIa** should be preferable. The anion **IIa** also abstracted the proton from the other MBUG to produce again the cyclic anion **I**, which attacks the carbonyl group of the dimer **III** to give a ring-opened urethane anion **IV**. Because its p*K*a should be estimated to be 24 and **IV** should be regarded as a weaker base than alkoxides, this step should favor the C—N scission. Because the acidity of the cyclic urethane is considered to be higher than the linear one, the anion **IV** abstracts the proton from the monomer to produce the cyclic anion **I** again. The propagation reaction should occur between the cyclic terminal group and **I**, and the resulting polyurethane should have one urea and one cyclic urethane unit at the initiation and propagation terminals, respectively. The m/z values of $[M + H]^+$ peaks in Figure 1 almost equal to simple multiples of 307.1 (molar mass of MBUG), which should support these terminal structure.

TABLE 3 pK_a values in DMSO of the related compounds

Compound	pK_a	References
	20.8	18
	24.2	18
	32.2	19
	44.0	20

Summary

Anionic polymerization of the five-membered cyclic urethane derived from D-glucosamine, MBUG, was examined. The polymerization with *t*-BuOK at 0 °C formed polyurethane having a relatively higher Mn without any decarbonylation in spite of the thermodynamically unfavorable nature known for the five-membered cyclic urethane. The mechanistic investigation indicates that the polymerization proceeds by a proton abstraction mechanism. The resulting polyurethane did not decompose below 260 °C and showed no glass-transition temperature below 210 °C. Because MBUG could be prepared from the naturally abundant D-glucosamine, poly(MBUG) might be regarded as a thermally stable polymer from renewable resources.

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