Anionic Ring-Opening Polymerization of a Novel Optically Active Bicyclic Lactam Synthesized from an Acidic Saccharide

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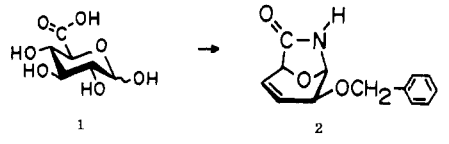
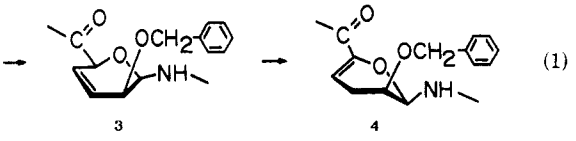
ABSTRACT: A new optically active bicyclic lactam, (1*S*,4*S*,5*R*)-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (**2**), was synthesized from the most common acidic monosaccharide, D-glucuronic acid (**1**) in 12% total yield. Anionic ring-opening polymerization of **2** proceeded at −60 to +25 °C in various solvents to give acetone-insoluble polymers. From the spectroscopic analyses, the polymer precipitated from the tetrahydrofuran solution during the polymerization at −40 °C was found to have a repeating unit containing a 5,6-dihydro-2*H*-pyran ring (**3**) and that obrained in the *N*,*N*-dimethylformamide homogeneous solution to have another unit with a 5,6-dihydro-4*H*-pyran ring (**4**), which was isomerized from **3**. The double bond in **3** rearranges through a polymeric anion formed by a proton abstraction in the later stage of the polymerization in the homogeneous solution.

Introduction

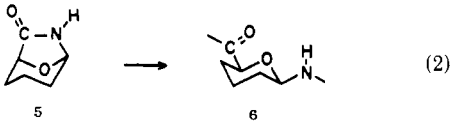
A bicyclic oxalactam, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (**5**), can be easily polymerized anionically under mild conditions such as at room temperature in dimethyl sulfoxide (Me_2SO), which is desirable for suppressing possible side reactions.[1-4] The resulting hydrophilic polyamide (**6**) has an acyllactam-type reactive end group, and it can be modified to various useful functional groups.[5-7] The high molecular weight polyamide **6** is easily cast to a hygroscopic membrane which has a high hydraulic permeability and a high permselectivity for aqueous solutes.[2,8] Therefore, bicyclic lactams having a skeleton similar to that of **5** may also have high polymerizability (see eqs 1 and 2).



1 **2**



3 **4** (1)

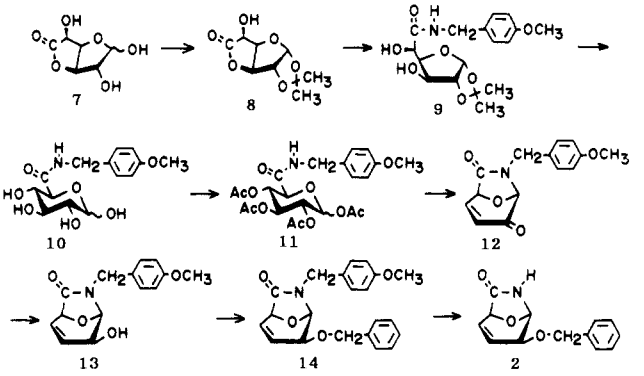


5 **6** (2)

Macromolecules derived from naturally occurring compounds such as polysaccharides and their repeating units, monosaccharides, are expected to be potentially biodegradable or biocompatible.[9,10] Various kinds of multicomponent materials containing polysaccharide sequences have been prepared.[11-15]

D-Glucuronic acid (**1**) is an acidic monosaccharide contained as an essential constituent in heteropolysaccharides such as chondroitin sulfate, hyaluronic acid, and glucuronoxylan.[16] In addition, **1** is apt to form the lactone, D-glucofuranurono-6,3-lactone (**7**) through its intramolecular cyclization, which is a commercially available crystalline compound. We are expected **7** to be an attractive starting material for polymer synthesis. If a bicyclic lactam having a skeleton similar to that of **5** is prepared from **7**, its ring-opening polymerization is expected to give a novel polyamide, as that of **5** does. The present investigation is concerned with the synthesis of an optically active bicyclic oxalactam, (1*S*,4*S*,5*R*)-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (**2**)[17] from **7** and its anionic ring-opening polymerization.

Scheme I



7 **8** **9** **10** **11** **12** **13** **14** **2**

Results and Discussion

Synthesis. An optically active bicyclic oxalactam, (1*S*,4*S*,5*R*)-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (**2**), was synthesized from D-glucofuranurono-6,3-lactone (**7**) through eight reaction steps as illustrated in Scheme I. The characteristic points in the present route are the temporary introduction of a *p*-methoxybenzyl group to the amide nitrogen atom in 1,2,3,4-tetra-*O*-acetyl-D-glucopyranuronamide in advance of its intramolecular cyclization (see compound **11**) and the elimination of the *p*-methoxybenzyl group in the final step, as described later.

According to the literature,[18] the anomeric hydroxyl group in **7** was first protected with an isopropylidene group. The subsequent reaction of 1,2-*O*-isopropylidene-D-glucofuranurono-6,3-lactone (**8**) with a small excess of *p*-methoxybenzylamine without catalyst in tetrahydrofuran (THF) at room temperature gave nearly quantitatively *N*-(*p*-methoxybenzyl)-1,2-*O*-isopropylidene-D-glucofuranuronamide (**9**). The reactivity of the lactone ring in **8** may be enhanced by the hydroxyl group adjacent to the lactone carbonyl group, as the lactone rings in D-glucaro-1,4:6,3-dilactone in its reaction with amines.[19]

Then the isopropylidene group in **9** was removed by hydrolysis in a mixture of trifluoroacetic acid and water (2:1, v/v) at room temperature. During the hydrolysis, the furanose ring in the glucuronamide was also converted

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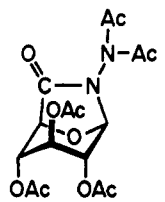
to its pyranose ring. The resulting colorless solid, *N*-(*p*-methoxybenzyl)-D-glucopyranuronamide (**10**), was acetylated with excess acetic anhydride and pyridine at room temperature to give a mixture of the α- and β-anomers of *N*-(*p*-methoxybenzyl)-1,2,3,4-tetra-*O*-acetyl-D-glucopyranuronamide (**11**). The α- and β-anomers could be isolated from the mixture by the repeated fractional reprecipitation and recrystallization, but their purification was troublesome. In the present investigation the mixture was used for the following reaction.

The acid-catalyzed intramolecular cyclization of the N-substituted glucuronamide **11** was attempted under various conditions and monitored by thin-layer chromatography. The cyclization needed the reflux of the reaction mixture at high temperature, by which a significant amount of **11** was forced to resinify. When **11** was refluxed in the presence of a strong acid such as trifluoromethanesulfonic acid in dilute chlorobenzene solution for 30 min, a bicyclic lactam having an unsaturated ketone group, (1*S*,5*R*)-*N*-(*p*-methoxybenzyl)-8-oxa-6-azabicyclo[3.2.1]-oct-2-ene-4,7-dione (**12**), was isolated in 38% yield from the reaction mixture. The elimination of acetyl groups presumably proceeds during the intramolecular cyclization.[20]

The carbonyl group in **12** was reduced to a hydroxyl group with sodium borohydride. The hydroxyl group in the resulting (1*S*,4*S*,5*R*)-4-hydroxy-*N*-(*p*-methoxybenzyl)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (**13**) was found to be preferentially directed to the equatorial position from the spectroscopic analysis (equatorial:axial = 98:2). The hydroxyl group was converted to a benzyl ether group, and finally the *p*-methoxybenzyl group was removed with ceric ammonium nitrate (the yield of (1*S*,4*S*,5*R*)-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (**2**) from **14** was 70%). The overall yield of **2** based on **7** was approximately 12%. The bicyclic lactam **2** formed colorless crystals melting at 145–146 °C. The structure was ascertained by elemental analysis, mass, IR, ^{1}H (see Figure 1), and ^{13}C NMR spectroscopies.

Previously Takeda et al.[21] synthesized a bicyclic lactam, (1*S*,2*R*,3*S*,4*S*,5*R*)-2,3,4-triacetoxy-*N*-(diacetylamino)-8-oxa-6-azabicyclo[3.2.1]octan-7-one (**15**), from **1** through



15

Ac, CH_3C–

a different route, but they did not describe the removal of the N-substituent. Therefore, **2** is the first N-unsubstituted polymerizable bicyclic lactam prepared from **1**, as far as we know.

From the results of the X-ray crystallographic analysis,[22] the internal bond angles of **2** were determined and compared with the corresponding ones of structurally related lactams[23–25] in Table I. The table indicates that several angles in every lactam significantly differ from the ideal ones for the sp^2 and sp^3 hybrid orbitals having no strain. Particularly, the large deviations of the internal angles in the bicyclic oxalactams, such as C(1)–C(7)–N(6), C(7)–C(1)–O(8), C(1)–O(8)–C(5), and N(6)–C(5)–O(8),

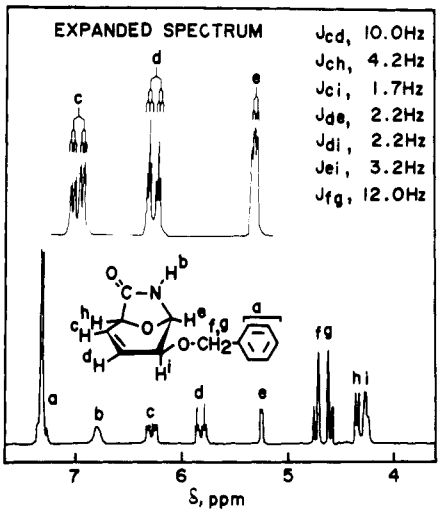
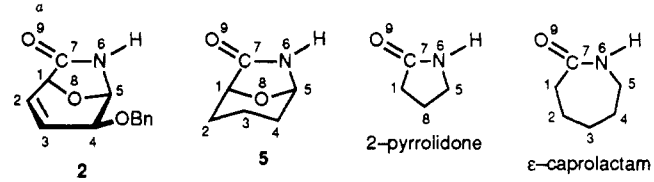


Figure 1. ^{1}H NMR spectrum of (1*S*,4*S*,5*R*)-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (**2**; $CDCl_3$, tetramethylsilane, room temperature, 200 MHz).

Table I
Internal Bond Angles (deg) in Various Lactams

bond angle[a]	lactam **2**[b,c]	lactam **5**[c,d]	2-pyrrolidone[c,e]	ε-caprolactam[c,f]
C(2)–C(1)–C(7)	106.1 (3)	109.9 (3)		113. 6 (2–3)
C(2)–C(1)–O(8)	109.1 (3)	108.8 (3)		
C(7)–C(1)–O(8)	101.6 (2)	102.4 (2)	104.7 (7)	
C(1)–C(2)–C(3)	118.6 (3)	110.8 (3)		113.9 (2–3)
C(2)–C(3)–C(4)	121.4 (3)	112.3 (3)		114.8 (2–3)
C(3)–C(4)–C(5)	110.1 (3)	110.8 (3)		113.9 (2–3)
C(4)–C(5)–N(6)	112.8 (3)	112.1 (3)		113.7 (2–3)
C(4)–C(5)–O(8)	107.9 (3)	108.6 (3)		
N(6)–C(5)–O(8)	102.4 (2)	101.3 (2)	105.8 (7)	
C(5)–N(6)–C(7)	110.3 (2)	110.1 (3)	109.0 (8)	125.5 (2–3)
C(1)–C(7)–N(6)	104.5 (2)	104.8 (3)	113.2 (8)	118.5 (2–3)
C(1)–O(8)–C(5)	101.8 (2)	102.3 (3)	106.7 (9)	



[b] Cited from ref 22. [c] The values in parenthese are standard deviations. [d] Cited from ref 23. [e] Cited from ref 24. [f] Cited from ref 25.

must be a reflection of the above-described high steric strain in the bicyclic skeleton. The most striking difference in the internal angles of **2** from those of **5** is found in the angle C(2)–C(1)–C(7), in which the additional strain is induced by the introduction of an internal double bond in the six-membered ring. From these results, the ring-opening ability of **2** can be predicted to be high, since the transition-state conformation of **2** having a rigid bicyclic skeleton is inferred to be very near that of its ground-state conformation.

Aminolysis of the *N*-Acetyl Derivative of 2. In order to understand the anionic polymerizability of lactams, the reactivity of their *N*-acyllactams should be estimated, because the *N*-acyllactams are known to accelerate the initiation and the growing chain ends are also of an acyllactam-type.[5,26,27] The reaction of *N*-acyllactams with *n*-butylamine proceeds quantitatively through the nucleophilic attack of the amine on either exo- or endocyclic carbonyl groups.[28,29] Therefore, the aminolysis of *N*-acyllactams can be used as a proper model reaction for discussion on the polymerizability of lactams.[28,29]

In the present investigation, the *N*-acetyl derivative of **2**, (1*S*,4*S*,5*R*)-*N*-acetyl-4-(benzyloxy)-8-oxa-6-azabicyclo-

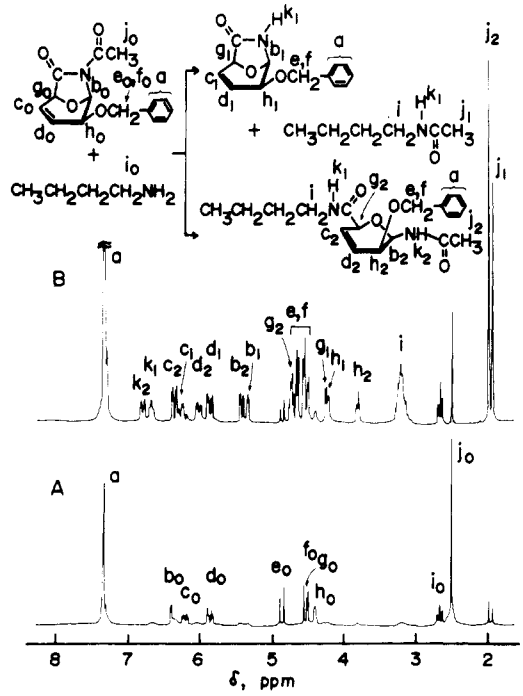
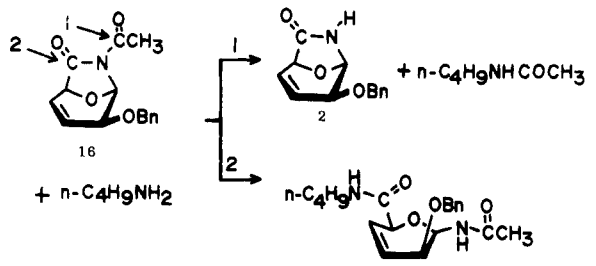


Figure 2. ^{1}H NMR spectra of the reaction mixture of (1*S*,4*S*,5*R*)-*N*-acetyl-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (**16**) with *n*-butylamine in deuterated chloroform at 27 °C for 90 min (A) and 760 min (B) (tetramethylsilane, room temperature, 200 MHz). Initial concentrations of *n*-butylamine and **16**: (a) 0.33 mol/L; (b) 0.29 mol/L.

Scheme II



[3.2.1]oct-2-en-7-one (**16**), was prepared, and the reaction of **16** with *n*-butylamine in deuterated chloroform at 27 °C was traced by ^{1}H NMR spectroscopy. As shown in Scheme II and Figure 2, the amine was found to react with both the exo- and endocyclic carbonyl groups in **16**. The aminolysis of the *N*-acetyl derivative of **5** also proceeded through the attack of both the exo- and endocyclic carbonyl groups. In contrast, only the exocyclic carbonyl group in *N*-acetyl-2-pyrrolidone reacted with the amine under the same conditions. These results are similar to those in the aminolysis of *N*-benzoyl derivatives of **5** and monocyclic lactams (2-pyrrolidone and ϵ-caprolactam) reported in the previous article.[28,29]

In order to estimate the reactivity of *N*-acetyllactams more quantitatively, the kinetic data determined by the NMR spectroscopic trace were analyzed by applying the expression for a simple second-order reaction, eq 3, where

$$(a - b)^{-1} \ln \{b(a - x)/a(b - x)\} = kt \qquad (3)$$

a and *b* are the initial concentrations of *n*-butylamine and *N*-acetyllactam, respectively, and *x* is the concentration of the product at time *t*. The value of *x* at each time was determined from the relative peak intensities in the expanded ^{1}H NMR spectrum.

As shown in Figure 3 and Table II, the value of the apparent rate constant *k* for the reaction of the endocyclic

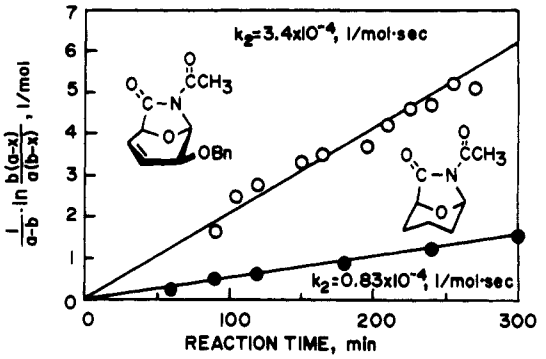


Figure 3. Kinetic analyses of the reaction of the endocyclic carbonyl group in *N*-acetyllactams with *n*-butylamine in deuterated chloroform at 27 °C: (a) 0.33 mol/L; (b) 0.29 mol/L. (○) (1*S*,4*S*,5*R*)-*N*-Acetyl-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (**16**). (●) *N*-Acetyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one.

Table II
Rate Constants of Aminolysis of *N*-Acetyllactams with *n*-Butylamine in Deuterated Chloroform at 25 °C[a]

	rate constant	
lactams	exocyclic carbonyl group	endocyclic carbonyl group
2	1.8×10^{-4}	3.4×10^{-4}
5	0.53×10^{-4}	0.83×10^{-4}
2-pyrrolidone	0.05×10^{-4}	0

[a] In L/mol·s.

carbonyl group in **16** was found to be 4 times larger than the corresponding one in the *N*-acetyl derivative of **5**. The *k* values for the exocyclic carbonyl groups in both the bicyclic skeletons were also by 1 order larger than that in *N*-acetyl-2-pyrrolidone. These results suggest that **2** as well as **5** has a high reactivity in the base-catalyzed ring-opening polymerization.

Polymerization. Taking account of the fact that the anionic ring-opening polymerization of the bicyclic lactam **5** proceeded at room temperature,[1-8] the unsaturated bicyclic lactam **2** was also expected to polymerize under mild conditions. In fact, the anionic polymerization of **2** by the use of potassium pyrrolidonate as a catalyst proceeded not only at 25 °C but also even at −60 °C as shown in Table III.

The polymerization at 25 °C in Me_2SO and 0 °C in a Me_2SO–THF mixed solvent gave a yellowish polymer, which was insoluble in any organic solvent. Therefore, the polymerization was tried at −40 or −60 °C in THF and at −40 °C in DMF. In the polymerization in THF, the resulting polymer was found to precipitate from the polymerization system, which was a main reason for the low polymer yield. On the other hand, the polymerization in DMF proceeded in a homogeneous phase and gave a yellowish powdered polymer in high yield. Both the polymers prepared in THF and DMF were soluble in chloroform, Me_2SO, DMF, *m*-cresol, 2,2,2-trifluoroethanol, and so on, although the solubility of the latter polymer in chloroform was lower than that of the former polymer. The number-average molecular weights of the resulting polymers were determined to be 5500–15 600 by GPC, and one of them (M_n 15 600) has a film-forming ability. Further optimization of the polymerization conditions should be required to obtain a higher molecular weight polymer.

The sign of the specific rotatory power of the polymer prepared in THF was found to be opposite from that of the polymer prepared in DMF; that is, the $[\alpha]^{25}_D$ values were −57.1° and +27.1°, respectively. This fact suggests that their structures differ from each other.

Table III
Polymerization of (1*S*,4*S*,5*R*)-4-(Benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (2)[a]

2, g	activator,[b] mol %	solvent, mL	temp, °C	time, h	yield, %	polym struct[c]	$[\alpha]^{25}_D$[d]	M_n[e]	M_w/M_n[e]	remark
0.30	5	Me_2SO 0.5	25	0.5	46	4				cross-linked
0.30	1	Me_2SO 0.3 THF 0.2	0	16	100	4				cross-linked
0.30	5	THF 0.5	−40	4	32	3		5 800	1.8	heterogeneous
0.30	5	THF 0.5	−60	4	31[f]	3	−57.4	5 500	1.4	heterogeneous
0.30	5	DMF 1.0	−40	0.5	75	3 + 4	−37.1	10 400	4.2	homogeneous
0.90	1	DMF 3.0	−40	4	93[g]	4	+27.1	15 600	6.0	homogeneous

[a] Potassium pyrrolidonate (2 mol %)/2. [b] *N*-Benzoyl derivative of 5. [c] 3, poly[(2*S*,5*S*,6*R*)-5-(benzyloxy)-5,6-dihydro-2*H*-pyran-2,6-diyliminocarbonyl]; 4, poly[(5*S*,6*R*)-5-(benzyloxy)-5,6-dihydro-4*H*-pyran-2,6-diyliminocarbonyl]. [d] Concentration, *c* 0.5 in chloroform. [e] By GPC in Me_2SO (standard: monodisperse polyamide prepared from 5). [f] Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.50; H, 5.67; N, 6.06. Found: C, 67.50; H, 5.66; N, 5.99. Melting point, 230 °C; decomposition point, 260 °C. [g] Anal. Calcd for $C_{13}H_{13}NO_3 \cdot {}^1/_3H_2O$: C, 65.79; H, 5.81; N, 5.91. Found: C, 65.76; H, 5.84; N, 6.06. Decomposition point, 260 °C.

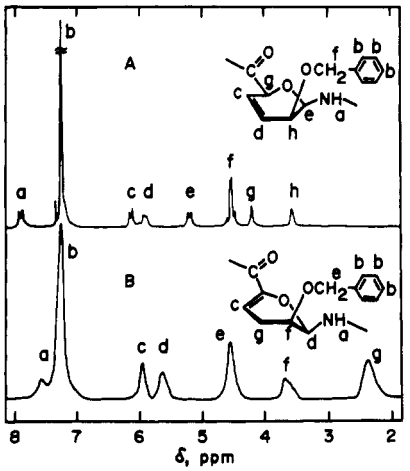


Figure 4. ^1H NMR spectra of polyamides obtained by anionic polymerization of (1*S*,4*S*,5*R*)-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (2) at −40 °C in THF (A) and DMF (B) ($CDCl_3$, tetramethylsilane, 50 °C, 270 MHz).

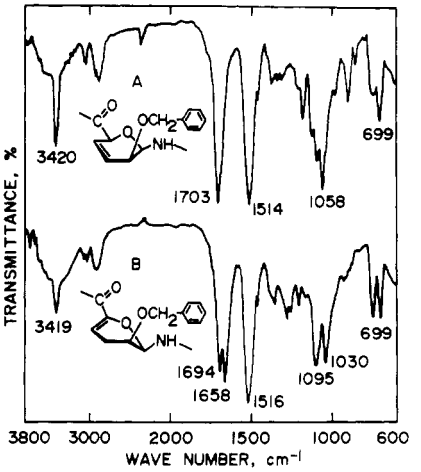


Figure 5. Infrared spectra of polyamides obtained by anionic polymerization of (1*S*,4*S*,5*R*)-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (2) at −40 °C in THF (A) and DMF (B) (KBr disk).

Polymer Structure. The data of the elemental analyses of both polymers prepared in THF and DMF were consistent with that of the monomer 2 (see the footnotes in Table III), which indicated that no elimination reaction occurred during the polymerization.

The ^1H NMR spectra in Figure 4 show that the structure of the polymer obtained in THF is quite different from that obtained in DMF. Their ^{13}C NMR spectra were also different from each other. Spectrum A in Figure 4 has eight signals, which correspond to those for monomer 2 in Figure 1, respectively. On the other hand, spectrum B is very different from spectrum A. Especially, signal g appearing at 2.3 ppm should give a key to the structural analysis.

As shown in Figure 5, both infrared spectra have strong bands due to the secondary amide groups around the wave numbers 1700 and 1510 cm^{-1}. The spectrum of the polymer obtained in DMF has an additional strong absorption band due to the vinyl ether group at 1658 cm^{-1}. Therefore, the polymer prepared in THF was determined to have a repeating unit 3 containing a 5,6-dihydro-2*H*-pyran ring, whereas the polymer prepared in DMF was determined to have another repeating unit 4 with a 5,6-dihydro-4*H*-pyran ring, which was isomerized from 3.

The polymer obtained in the polymerization of a relatively short time in DMF contained both the structural units 3 and 4 (Table III). Therefore, the isomerization probably proceeds in the later stage of the polymerization. In addition, the isomerization did not occur in the polymerization in the THF heterogeneous solution. This means that the dissolution of the polymer in a homogeneous polymerization system is necessary for the isomerization of the repeating unit.

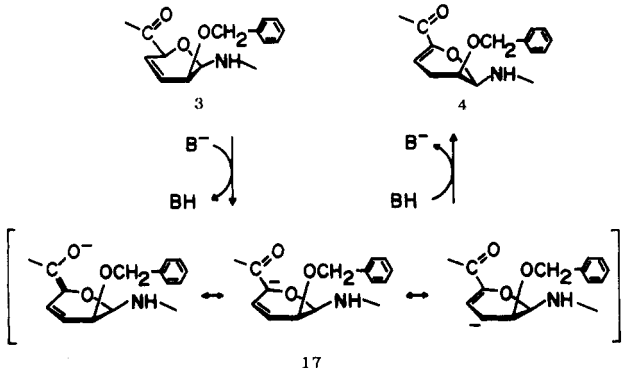
A main side reaction observed in the later stage of the polymerization in the homogeneous phase is a proton abstraction from the resulting polymer chain. As a matter of fact, the value of pK_a for the α-methine proton adjacent to the amide–carbonyl group in the repeating unit of 3 can be speculated to be much lower than that for the corresponding bridgehead methine proton in the monomer 2 having the rigid bicyclic molecular skeleton as in the case of the bicyclic lactam 5.[4] The polymeric anion 17 produced by the proton abstraction at the α-methine carbon atom in 3 is expected to be relatively stable, because the electronic charge in 17 is delocalized to the neighboring amide group and double bond as shown in Scheme III. Through the polymeric anion, the double bond rearranges to form a thermodynamically stable repeating unit 4.

From the infrared spectroscopic analysis, the polymer obtained in the polymerization at 25 or 0 °C was found to have essentially the isomerized repeating unit 4. At higher temperature the rearrangement reaction must be fast and the repeating unit 3 is immediately isomerized to the unit 4.

As described before, the polyamide obtained in the polymerization at higher temperature was insoluble in any organic solvent. Therefore, the polymer is thought to have cross-linked during or after polymerization, although the detailed microstructure of the cross-linked points has not been clear yet.

In summary, the optically active bicyclic lactam 2 was successfully synthesized from D-glucuronic acid by a new

Scheme III



route. As anticipated from its highly strained bicyclic structure, **2** showed a high reactivity in its anionic ring-opening polymerization. Since the resulting polymer contains a labile C=C double bond in its repeating unit, the anionic polymerization should be carried out under carefully controlled reaction conditions in order to obtain soluble polyamides of regular structure. Thus, in the polymerization at or above 0 °C, a cross-linking reaction inevitably occurred to give insoluble products. The polymerization of **2** in THF at or below −40 °C, proceeded in a heterogeneous state, giving the polyamide **3** containing a 5,6-dihydro-2*H*-pyran ring in its repeating unit. The polymerization in a homogeneous DMF solution was accompanied by the rearrangement of the C=C double bond and eventually provided the polyamide **4** entirely composed of 5,6-dihydro-4*H*-pyran rings. The biodegradability and biocompatibility of the resulting polymer are subjects to be investigated in the future.

Experimental Section

Preparation of *N*-(*p*-Methoxybenzyl)-1,2-*O*-isopropylidene-D-glucofuranuronamide (9). First the anomeric and its neighboring hydroxyl groups in D-glucofuranurono-6,3-lactone (**7**) were protected with an isopropylidene group by the same method as described in the literature (yield 87%).[18] To a solution of the resulting 1,2-*O*-isopropylidene-D-glucofuranurono-6,3-lactone (**8**; 41.3 g, 191 mmol) in 200 mL of THF was added *p*-methoxybenzylamide (27.5 g, 200 mmol) dropwise with stirring at room temperature for 20 min.[30] The reaction mixture was stirred at room temperature for 4 h. After evaporation of the organic solvent, the viscous residue was dissolved in 50 mL of ethyl acetate, and then 150 mL of *n*-hexane was added to the solution. The resulting colorless crystals were collected and dried in vacuo. The yield of **9** was 63.4 g (94%): mp 114–115 °C; $[\alpha]^{25}_D$ −10.5° (chloroform, *c* 1.0); IR (KBr disk) 3500, 3300, 3200 (ν_{NH} (amide) and ν_{OH}), 1640 ($\nu_{C=O}$, amide) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (t, J(N*H*–CH_2) = 5.9 Hz, 1 H, amide N*H*), 7.17 (d, J(ortho–meta) = 11.6 Hz, 2 H, ortho), 6.84 (d, J(ortho–meta) = 11.6 Hz, 2 H, meta), 5.91 (d, $J(^1CH–^2CH)$ = 3.6 Hz, 1 H, ^1CH), 4.73 (br s, 2 H, O*H*), 4.48 (d, $J(^1CH–^2CH)$ = 3.6 Hz, 1 H, ^2CH), 4.40 (d, J(N*H*–CH_2) = 5.9 Hz, 2 H, CH_2), 4.39 (d, 1 H, ^3CH), 4.33 (d, $J(^4CH–^5CH)$ = 3.0 Hz, 1 H, ^5CH), 4.29 (dd, $J(^3CH–^4CH)$ = 6.3 Hz, $J(^4CH–^5CH)$ = 3.0 Hz, 1 H, ^4CH), 3.76 (s, 3 H, CH_3O), 1.44, 1.28 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 172.1 (*C*=O), 159.0 (Ar ^4C), 129.7 (Ar ^1C), 128.8 (Ar ^2C and ^6C), 114.1 (Ar ^3C and ^5C), 112.1 (quaternary carbon), 105.2 (^1C), 85.1 (^2C), 81.2 (^4C), 75.2 (^5C), 69.5 (^3C), 55.3 (CH_3O), 42.9 (CH_2), 26.9 26.3 (isopropylidene CH_3).

Preparation of *N*-(*p*-Methoxybenzyl)-D-glucopyranuronamide (10). In a three-necked round-bottom flask, *N*-(*p*-methoxybenzyl)-1,2-*O*-isopropylidene-D-glucofuranuronamide (**9**; 63.4 g, 179 mmol) was added to a mixture of 200 mL of trifluoroacetic acid and 100 mL of deionized water by reference to Christensen's method.[31] The solution was stirred at room temperature for 3 h. After removal of the solvents, the residue was poured into 900 mL of acetone and the colorless precipitate was obtained in 85% yield (49.9 g). The mole ratio of α- and β-anomers of **10** was 0.49:0.51 at equilibrium in aqueous solution: mp 154–155 °C; $[\alpha]^{25}_D$ +28.4° (water, *c* 1.0); ^1H NMR (D_2O) δ 7.03 (d, J(ortho–meta) = 8.0 Hz, 2 H, ortho), 6.70 (d, J(ortho–meta) = 8.0 Hz, 2 H, meta), 5.08 (d, $J(^1CH_{eq}–^2CH)$ = 3.4 Hz, 0.5 H, $^1CH_{eq}$), 4.48 (d, $J(^1CH_{ax}–^2CH)$ = 7.8 Hz, 0.5 H, $^1CH_{ax}$), 4.70 (s, 5 H, O*H*), 4.12 (s, 2 H, CH_2), 4.08–3.07 (m, 4 H, ^2CH, ^3CH, ^4CH, and ^5CH), 3.55 (s, 3 H, CH_3O); ^{13}C NMR (D_2O) δ 171.2, 170.4 (*C*=O), 158.2 (Ar ^4C), 130.3 (Ar ^1C), 130.0 (Ar ^2C and ^6C), 114.4 (Ar ^3C and ^5C), 96.4 (β-^1C), 92.7 (α-^1C), 75.7, 75.6, 74.1, 72.8, 72.0, 71.8, 71.4 (^2C, ^3C, ^4C, ^5C), 55.7 (CH_3O), 42.6 (CH_2).

Preparation of *N*-(*p*-Methoxybenzyl)-1,2,3,4-tetra-*O*-acetyl-D-glucopyranuronamide (11). A mixture of *N*-(*p*-methoxybenzyl)-D-glucopyranuronamide (**10**; 43.7 g, 139 mmol), acetic anhydride (217 g, 2.13 mol), and pyridine (197 g, 2.48 mol) was stirred in a 1-L three-necked round-bottom flask at room temperature for 1 day. After 200 mL of ethanol was added to the reaction mixture in order to consume the excess acetic anhydride, the organic solvents were removed from the mixture with a rotary evaporator. To the residual amber viscous oil was added 100 mL of water, and the mixture was extracted with four 200-mL portions of chloroform. The combined organic layers were dried over anhydrous sodium carbonate and then concentrated again under reduced pressure. To the viscous residue was added 250 mL of 2-propanol with stirring. The resulting colorless powder, the crude β-anomer of **11**, was collected on a glass filter, washed with 2-propanol, and dried in vacuo: yield 34.4 g (52%). The filtrate was concentrated and added to 250 mL of diethyl ether to precipitate the crude α-anomer: yield 9.4 g (14%). Each crude anomer was recrystallized from 2-propanol.

β-Anomer: mp 161.5–162.5 °C; $[\alpha]^{25}_D$ +29.2° (chloroform, *c* 1.0); IR (KBr disk) 3400 (ν_{NH}), 1740 ($\nu_{C=O}$, ester), 1680 ($\nu_{C=O}$, amide), 1530 (δ_{NH}, amide), 1220 and 1040 (ν_{COC}, ester) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.19 (d, J(ortho–meta) = 8.3 Hz, 2 H, ortho), 6.86 (d, J(ortho–meta) = 8.3 Hz, 2 H, meta), 6.69 (t, J(N*H*–CH_2) = 6.1 Hz, 1 H, amide N*H*), 5.76 (d, $J(^1CH_{ax}–^2CH)$ = 8.1 Hz, 1 H, $^1CH_{ax}$), 5.33 (t, $J(^2CH–^3CH)$ = $J(^3CH–^4CH)$ = 9.1 Hz, 1 H, ^3CH), 5.23 (t, $J(^3CH–^4CH)$ = $J(^4CH–^5CH)$ = 9.1 Hz, 1 H, ^4CH), 5.09 (dd, $J(^1CH_{ax}–^2CH)$ = 8.1 Hz, $J(^2CH–^3CH)$ = 9.1 Hz, 1 H, ^2CH), 4.40, 4.26 (dd, J(N*H*–CH_2) = 6.1 Hz, J(gem CH_2) = 14.5 Hz, 1 H, one of gem CH_2), 4.11 (d, $J(^4CH–^5CH)$ = 9.1 Hz, 1 H, ^5CH), 3.78 (s, 3 H, CH_3O), 2.07, 2.06, 2.03, 2.02 (s, 3 H, acetyl CH_3); ^{13}C NMR ($CDCl_3$) δ 169.7, 169.5, 169.2, 168.7, 165.7 (*C*=O), 159.0 (Ar ^4C), 129.5 (Ar ^1C), 129.2 (Ar ^2C and ^6C), 114.0 (Ar ^3C and ^5C), 91.2 (β-^1C), 72.9 (^5C), 71.9 (^3C), 70.1 (^2C), 69.0 (^4C), 55.2 (CH_3O), 42.4 (CH_2), 20.7, 20.5 (acetyl CH_3).

α-Anomer: mp 107.5–110.5 °C; $[\alpha]^{25}_D$ +106.4° (chloroform, *c* 1.0); IR (KBr disk) 3400 (ν_{NH}), 1750 ($\nu_{C=O}$, ester), 1680 ($\nu_{C=O}$, amide), 1530 (δ_{NH}, amide), 1210, 1080, 1040 (ν_{COC}, ester) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.19 (d, J(ortho–meta) = 8.3 Hz, 2 H, ortho), 6.86 (d, J(ortho–meta) = 8.3 Hz, 2 H, meta), 6.69 (t, J(N*H*–CH_2) = 5.6 Hz, 1 H, amide N*H*), 6.33 (d, $J(^1CH_{eq}–^2CH)$ = 3.7 Hz, 1 H, $^1CH_{eq}$), 5.33 (t, $J(^2CH–^3CH)$ = $J(^3CH–^4CH)$ = 9.8 Hz, 1 H, ^3CH), 5.21 (dd, $J(^3CH–^4CH)$ = 9.8 Hz, $J(^4CH–^5CH)$ = 10.1 Hz, 1 H, ^4CH), 5.09 (dd, $J(^1CH_{eq}–^2CH)$ = 3.7 Hz, $J(^2CH–^3CH)$ = 9.8 Hz, 1 H, ^2CH), 4.41, 4.25 (dd, J(N*H*–CH_2) = 5.6 Hz, J(gem CH_2) = 14.6 Hz, 1 H, one of gem CH_2), 4.34 (d, $J(^4CH–^5CH)$ = 10.1 Hz, 1 H, ^5CH), 3.79 (s, 3 H, CH_3O), 2.17, 2.16, 2.03, 2.01 (s, 3 H, acetyl CH_3); ^{13}C NMR ($CDCl_3$) δ 169.8, 169.7, 168.8, 166.2 (*C*=O), 159.2 (Ar ^4C), 129.6 (Ar ^1C), 129.3 (Ar ^2C and ^6C), 114.2 (Ar ^3C and ^5C), 88.3 (^1C), 70.4 (^5C), 69.2 (^4C), 69.0 (^2C and ^3C), 55.3 (CH_3O), 42.6 (CH_2), 20.7, 20.6, 20.4 (acetyl CH_3).

Preparation of (1*S*,5*R*)-*N*-(*p*-Methoxybenzyl)-8-oxa-6-azabicyclo[3.2.1]oct-2-ene-4,7-dione (12). To a solution of *N*-(*p*-methoxybenzyl)-1,2,3,4-tetra-*O*-acetyl-D-glucopyranuronamide (**11**; 4.81 g, 10 mmol) and a trace amount of hydroquinone in 700 mL of chlorobenzene was added 0.15 g (1 mmol) of trifluoromethanesulfonic acid with stirring at 132 °C, and the mixture was refluxed for 0.5 h. After the addition of 10 g of anhydrous sodium carbonate for quenching, excess carbonate was filtrated off and the organic solvent was evaporated. The residue was offered to the elutional fractionation through a preparative silica gel column (Fuji Davison, silica gel BW-820MH), using a mixture of chloroform and ethyl acetate (5:1, v/v) as eluent. Slightly-colored crystals of **12** were obtained in 38% yield (0.97 g). After recrystallization from diethyl ether, **12** was characterized as follows: mp 92.5–93.5 °C; $[\alpha]^{25}_D$ −733°

(chloroform, c 1.0). MW 259 (m/e of parent peak in mass specturm); IR (KBr disk) 1722 ($\nu_{C=O}$, ketone and amide), 1242 (ν_{COC}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36 (dd, $J(^2CH-^3CH)$ = 9.9 Hz, $J(^1CH-^2CH)$ = 4.6 Hz, 1 H, ^2CH), 7.18 (d, J(ortho–meta) = 8.6 Hz, 2 H, ortho), 6.87 (d, J(ortho–meta) = 8.6 Hz, 2 H, meta), 6.00 (dd, $J(^2CH-^3CH)$ = 9.9 Hz, $J(^3CH-^5CH)$ = 1.7 Hz, 1 H, ^3CH), 5.00 (d, $J(^3CH-^5CH)$ = 1.7 Hz, 1 H, ^5CH), 4.77 (d, $J(^1CH-^2CH)$ = 4.6 Hz, 1 H, ^1CH), 4.69, 3.99 (d, J(gem CH_2) = 15.2 Hz, 1 H, one of gem CH_2), 3.79 (s, 3 H, CH_3O); ^{13}C NMR ($CDCl_3$) δ 185.8 (C=O, ketone), 169.9 (C=O, lactam), 159.3 (Ar ^4C), 145.6 (^2C), 129.6 (Ar ^2C and ^6C), 126.6 (^3C), 126.1 (Ar ^1C), 114.1 (Ar ^3C and ^5C), 89.8 (^5C), 74.4 (^1C), 55.2 (CH_3O), 43.5 (CH_2). Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.83; H, 5.00; N, 5.36.

Preparation of (1S,4S,5R)-4-Hydroxy-N-(p-methoxybenzyl)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (13). To a solution of (1S,5R)-N-(p-methoxybenzyl)-8-oxa-6-azabicyclo[3.2.1]oct-2-ene-4,7-dione (12; 2.33 g, 9.0 mmol) in 70 mL of methanol was added 0.34 g (9.0 mmol) of sodium borohydride at 7 °C.[32] After the solution was stirred at the same temperature for 30 min, 10 mL of 3.6 N ammonium chloride aqueous solution was added to the reaction mixture for quenching. Methanol was removed with a rotary evaporator, and the residual solution was extracted with chloroform. The organic layers were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The resulting colorless powder was collected and dried in vacuo: yield 2.32 g (99%); IR (KBr disk) 3300 (ν_{OH}), 1680 ($\nu_{C=O}$, amide), 1240 (ν_{COC}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (d, J(ortho–meta) = 8.7 Hz, 2 H, ortho), 6.86 (d, J(ortho–meta) = 8.7 Hz, 2 H, meta), 6.27 (ddd, $J(^2CH-^3CH)$ = 9.9 Hz, $J(^1CH-^2CH)$ = 4.1 Hz, $J(^2CH-^4CH)$ = 1.5 Hz, 1 H, ^2CH), 5.77 (ddd, $J(^2CH-^3CH)$ = 9.9 Hz, $J(^3CH-^4CH)$ = $J(^3CH-^5CH)$ = 2.3 Hz, 1 H, ^3CH), 5.16 (dd, $J(^4CH-^5CH)$ = 4.1 Hz, $J(^3CH-^5CH)$ = 2.3 Hz, 1 H, ^5CH), 4.90, 4.20 (d, J(gem CH_2) = 15.1 Hz, 1 H, one of gem CH_2), 4.52 (m, 1 H, ^4CH), 4.42 (d, $J(^1CH-^2CH)$ = 4.1 Hz, 1 H, ^1CH), 3.78 (s, 3 H, CH_3O), 3.03 (br s, 1 H, OH); ^{13}C NMR ($CDCl_3$) δ 173.8 (C=O, lactam), 159.0 (Ar ^4C), 130.1 (^2C), 129.2 (Ar ^2C and ^6C), 128.1 (^3C), 127.6 (Ar ^1C), 114.1 (Ar ^3C and ^5C), 87.2 (^5C), 73.1 (^1C), 64.8 (^2C), 55.2 (CH_3O), 45.8 (CH_2).

Preparation of (1S,4S,5R)-4-(Benzyloxy)-N-(p-methoxybenzyl)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (14). Under dry nitrogen (1S,4S,5R)-4-hydroxy-N-(p-methoxybenzyl)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (13; 2.32 g, 8.9 mmol) and benzyl bromide (1.59 g, 9.3 mmol) were dissolved in 30 mL of THF in a round-bottom flask. Then 0.37 g (9.3 mmol) of 60% sodium hydride in an oil dispersion was added to the solution at room temperature, and the mixture was stirred for 3 h.[33] After quenching with 20 mL of water, the reaction mixture was extracted with chloroform. The chloroform layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to yield colorless crude solid 14: yield 3.3 g (~100%); ^1H NMR ($CDCl_3$) δ 7.32 (m, 5 H, phenyl CH in benzyl), 7.13 (d, J(ortho–meta) = 8.7 Hz, 2 H, ortho in methoxybenzyl), 6.84 (d, J(ortho–meta) = 8.7 Hz, 2 H, meta in methoxybenzyl), 6.29 (ddd, $J(^2CH-^3CH)$ = 9.9 Hz, $J(^1CH-^2CH)$ = 4.3 Hz, $J(^2CH-^4CH)$ = 1.7 Hz, 1 H, ^2CH), 5.88 (ddd, $J(^2CH-^3CH)$ = 9.9 Hz, $J(^3CH-^4CH)$ = $J(^3CH-^5CH)$ = 2.2 Hz, 1 H, ^3CH), 5.18 (dd, $J(^4CH-^5CH)$ = 3.9 Hz, $J(^3CH-^5CH)$ = 2.2 Hz, 1 H, ^5CH), 5.05, 4.04 (d, J(gem CH_2) = 15.2 Hz, 1 H, one of gem CH_2 in methoxybenzyl), 4.65, 4.55 (d, J(gem CH_2) = 11.7 Hz, 1 H, one of gem CH_2 in benzyl), 4.43 (d, $J(^1CH-^2CH)$ = 4.3 Hz, 1 H, ^1CH), 4.29 (m, 1 H, ^4CH), 3.77 (s, 3 H, CH_3O).

Preparation of (1S,4S,5R)-4-(Benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (2). To a solution of (1S,4S,5R)-4-(benzyloxy)-N-(p-methoxybenzyl)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (14; 2.83 g, 8.05 mmol) in 70 mL of acetonitrile was added an aqueous solution of ceric ammonium nitrate (13.3 g, 24.2 mmol) in 7 mL of water at room temperature. The mixture was stirred for 3 h, and then 30 mL of an aqueous solution containing sodium acetate (11.9 g, 145 mmol) was added to the reaction mixture for termination. After removal of acetonitrile, the residue was extracted with four 100-mL portions of chloroform. The chloroform layers were dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and the residue was fractionated through a preparative silica gel column, eluted with a mixture of chloroform and ethyl acetate (3:2, v/v). The crude 2 (yield 1.30 g (70%)) was crystallized from diethyl ether: mp 145–146 °C; $[\alpha]^{25}_D$ –297° (chloroform, c 1.0). MW 231 (m/e of parent peak in mass spectrum); IR (KBr disk) 3170 (ν_{NH}, amide), 1725 ($\nu_{C=O}$, amide), 1689 ($\nu_{C=O}$), 1094 (ν_{COC}) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33 (m, 5 H, phenyl CH in benzyl), 6.70 (br s, 1 H, lactam NH), 6.28 (ddd, $J(^2CH-^3CH)$ = 10.0 Hz, $J(^1CH-^2CH)$ = 4.2 Hz, $J(^2CH-^4CH)$ = 1.7 Hz, 1 H, ^2CH), 5.87 (ddd, $J(^2CH-^3CH)$ = 10.0 Hz, $J(^3CH-^4CH)$ = $J(^3CH-^5CH)$ = 2.2 Hz, 1 H, ^3CH), 5.32 (dd, $J(^4CH-^5CH)$ = 3.2 Hz, $J(^3CH-^5CH)$ = 2.2 Hz, 1 H, ^5CH), 4.70, 4.53 (d, J(gem CH_2) = 12.0 Hz, 1 H, one of gem CH_2), 4.29 (d, $J(^1CH-^2CH)$ = 4.2 Hz, 1 H, ^1CH), 4.22 (m, 1 H, ^4CH); ^{13}C NMR ($CDCl_3$) δ 176.0 (C=O, lactam), 137.5 (Ar ^1C), 129.9 (^2C), 128.5, 128.0, 127.7 (Ar ^2C, ^3C, ^4C, ^5C, and ^6C), 128.0 (^3C), 84.5 (^5C), 72.0 (CH_2 and ^1C), 70.4 (^4C). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.50; H, 5.67; N, 6.06. Found: C, 67.43; H, 5.56; N, 6.15.

Preparation of (1S,4S,5R)-N-Acetyl-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (16). Under dry nitrogen acetyl chloride (0.14 g, 1.7 mmol) was added to a solution of (1S,4S,5R)-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (2; 0.20 g, 0.86 mmol) in 1 mL of pyridine at room temperature, and the solution was stirred for 3 h. Then the reaction was quenched by the addition of deionized water, and the mixture was extracted with diethyl ether. The solvent evaporated under reduced pressure, and the residue was offered to the elutional fractionation through a preparative silica gel column using a mixture of chloroform and ethyl acetate (5:1, v/v) to yield a colorless viscous oil: yield 0.11 g (48%); ^1H NMR ($CDCl_3$) δ 7.33 (m, 5 H, phenyl CH in benzyl), 6.39 (dd, $J(^4CH-^5CH)$ = 3.7 Hz, $J(^3CH-^5CH)$ = 1.7 Hz, 1 H, ^5CH), 6.20 (ddd, $J(^2CH-^3CH)$ = 9.8 Hz, $J(^1CH-^2CH)$ = 4.4 Hz, $J(^2CH-^4CH)$ = 1.5 Hz, 1 H, ^2CH), 5.85 (ddd, $J(^2CH-^3CH)$ = 9.8 Hz, $J(^3CH-^4CH)$ = $J(^3CH-^5CH)$ = 1.7 Hz, 1 H, ^3CH), 4.87, 4.54 (d, J(gem CH_2) = 11.5 Hz, 1 H, one of gem CH_2), 4.52 (d, $J(^1CH-^2CH)$ = 4.4 Hz, 1 H, ^1CH), 4.41 (m, 1 H, ^4CH), 2.51 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 170.9, 169.1 (C=O), 137.2 (Ar ^1C), 130.1 (^2C), 128.3, 127.8, 127.7 (Ar ^2C, ^3C, ^4C, ^5C, and ^6C), 126.3 (^3C), 84.9 (^5C), 73.9 (^1C), 72.0 (CH_2), 70.3 (^4C), 24.1 (CH_3).

Polymerization Procedure. Certain amounts of (1S,4S,5R)-4-(benzyloxy)-8-oxa-6-azabicyclo[3.2.1]oct-2-en-7-one (2) and N-benzoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one were charged into a tube equipped with a breakable ampule containing potassium pyrrolidonate. Then the tube was connected to a high-vacuum line to dry the contents. After a certain amount of the purified solvent was distilled in the tube in the vacuum-line system, the tube was sealed and held in a constant-temperature bath. Through the crushed breakable seal, potassium pyrrolidone was thrown into the solution with stirring. After polymerization, the tube was opened and a small amount of acetic acid was added to the system for termination. The contents of the tube was poured into a large amount of acetone, and the resulting yellowish product was collected on a glass filter. The product was purified by repeated reprecipitation and dried in vacuo.

Instruments. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX-200 and EX-270 Fourier transform high-resolution spectrometer. Infrared spectra and optical rotation were measured with a Jasco A-3 spectrometer and a DIP-181 digital polarimeter, respectively. Mass spectra were taken with a JEOL JMS-D100 spectrometer. The molecular weights of the polymers were estimated by using a Jasco Model DIP-1 high-performance liquid chromatograph (column, Shodex KF 803 → 804, 8φ × 600 mm; solvent Me_2SO, 0.4 mL/min).

References and Notes

(1) Sumitomo, H.; Hashimoto, K. *Macromolecules* **1977**, *10*, 1327.
(2) Hashimoto, K.; Sumitomo, H. *Macromolecules* **1980**, *13*, 786.
(3) Hashimoto, K.; Sumitomo, H.; Washio, A. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 1915.
(4) Hashimoto, K.; Sumitomo, H.; Shinoda, H.; Washio, A. *J. Polym. Sci., Polym. Lett.* **1989**, *27*, 307.
(5) Hashimoto, K.; Sumitomo, H.; Shinoda, H. *Polym. J.* **1988**, *20*, 321.
(6) Hashimoto, K.; Sumitomo, H.; Kawasumi, M. *Polym. Bull.* **1984**, *11*, 121.
(7) Hashimoto, K.; Sumitomo, H. *Polym. J.* **1983**, *15*, 547.
(8) Hashimoto, K.; Sumitomo, H.; Yamamori, H. *Polym. J.* **1987**, *19*, 1139.

(9) Huang, S. J. In *Encyclopedia of Polymer Science and Technology*, 2nd ed.; Mark, H., et al., Eds.; Wiley: New York, 1985; Vol. 2, p 220.
(10) Lyman, D. J.; Rowland, S. M. In *Encyclopedia of Polymer Science and Technology*, 2nd ed.; Mark, H., et al., Eds.; Wiley: New York, 1985; Vol. 2, p 267.
(11) Kumar, G. S.; Kalpagam, V.; Nandi, U. S. *J. Macromol. Sci., Rev.* **1982-3**, *C22*, 225.
(12) *Cellulose—Structural and Functional Aspects*; Kennedy, J. F., Phillips, G. O., Williams, P. A., Eds.; Ellis Horwood: Chichester, U.K., 1989.
(13) *Cellulose and Its Utilization*; Inagaki, H., Phillips, G. O., Eds.; Elsevier: London, 1989.
(14) Hashimoto, K.; Imanishi, S.; Okada, M.; Sumitomo, H. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 1271.
(15) Hashimoto, K.; Imanishi, S.; Okada, M.; Sumitomo, H. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 211.
(16) MacGregor, E. A.; Greenwood, C. T. *Polymers in Nature*; Wiley: New York, 1980; p 240.
(17) In the present paper, bicyclic oxalactams and the polyamides prepared from D-glucuronic acid are named according to IUPAC nomenclature but their precursors are named as derivatives of D-glucuronic acid.
(18) Owen, L. N.; Peat, S.; Jones, W. J. G. *J. Chem. Soc.* **1941**, 339.
(19) Hashimoto, K.; Okada, M.; Honjou, N. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 393.
(20) Hashimoto, K.; Mori, K.; Okada, M. *Chem. Lett.* **1991**, 2223.
(21) Takeda, Y.; Akimoto, T.; Kyogoku, Y. *Carbohydr. Res.* **1982**, *106*, 175.
(22) Yamane, T.; Matsueda, E.; Ashida, T.; Hashimoto, K.; Okada, M. *Bull. Chem. Soc. Jpn.*, to be submitted.
(23) Gu, Y.; Yamane, T.; Ashida, T.; Hashimoto, K.; Sumitomo, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2085.
(24) Harata, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2451.
(25) Winkler, F. K.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1975**, *31*, 268.
(26) Sekiguchi, H. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: London, 1984; Vol. 2, Chapter 12, p 809.
(27) Sebenda, J. *J. Macromol. Sci., Chem.* **1972**, *6*, 1145.
(28) Hashimoto, K.; Sumitomo, H.; Washio, A. *Polym. J.* **1988**, *20*, 615.
(29) Stehlicek, J.; Sebenda, J. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2524.
(30) Fieser, M.; Fieser, L. F.; Toromanoff, E.; Hirata, Y.; Heymann, H.; Tefft, M.; Bhattacharya, S. *J. Am. Chem. Soc.* **1956**, *78*, 2825.
(31) Christensen, J. E.; Goodman, L. *Carbohydr. Res.* **1968**, *7*, 510.
(32) Iqbal, K.; Jackson, W. R. *J. Chem. Soc. C* **1968**, 616.
(33) Czernecki, S.; Georgoulis, C.; Provelenghiou, C. *Tetrahedron Lett.* **1976**, 3535.