ing as TCNQ.

Copolymerization of BMI with BCQ. In order to estimate the monomer reactivity of BMI, copolymerization of BMI was carried out with a highly conjugative, electron-accepting monomer, 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ), in toluene at 60 °C. Because the homopolymerizations of BMI and BCQ are reluctantly influenced by depolymerization, their monomer concentrations were employed in copolymerization to be about 2 or 3 times as high as their equilibrium monomer concentrations. The results of the copolymerization are summarized in Table III, and their composition diagram is shown in Figure 12. The results were applicable without serious deviation to the intersection[10] and Kelen–Tüdös[11] methods to obtain monomer reactivity ratios, r_1(BMI) = 0.006 ± 0.005, r_2 = 7.3 ± 2.0 at 60 °C. The Alfrey–Price Q–e values of BMI were calculated by using the observed monomer reactivity ratios with Q and e values (9.3, +0.95) of BCQ[5] to be Q = 4.09 and e = +2.26. It is obvious that BMI is lower conjugatively (lower general reactivity) and much more electron accepting than BCQ.

Finally, it can be pointed out that *N*,7,7-tricyanobenzoquinone methide imine (BMI) is the most strongly electron-accepting monomer having homopolymerizability at the moment.

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Synthesis and Ring-Opening Polymerization of Novel Bicyclic Oxalactams. 2-Oxa-6-azabicyclo[2.2.2]octan-5-one

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ABSTRACT: A new bicyclic lactam, 2-oxa-6-azabicyclo[2.2.2]octan-5-one (2,6-BOL), was synthesized starting from acrolein and dimethyl malonate through a six-step reaction sequence. The anionic polymerization of 2,6-BOL using potassium pyrrolidonate and *N*-benzoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one as initiator and activator, respectively, at different temperatures ranging from 50 to 120 °C did not afford polyamide but a dimeric adduct (**9**) in low yield. Cationic polymerization of 2,6-BOL was initiated with trifluoromethanesulfonic acid and bis[(trifluoromethyl)sulfonyl]methane in dichloromethane and hexafluoroisopropyl alcohol at temperatures above −20 °C to yield powdery oligomers with molecular weights of several hundreds. Spectroscopic analysis disclosed that the oligomers were oligoethers containing 3,6-linked 2-piperidinone rings, which were produced by selective ring-opening reaction of 2,6-BOL at the C(1)–O(2) bond. The specific ring-opening polymerization behavior of 2,6-BOL is discussed in comparison with that of its structural isomer, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (8,6-BOL).

Introduction

Ring-opening polymerization of heterobicyclic compounds containing two or more heteroatoms in their ring skeletons provides a convenient and effective approach to designing specialty polymers of well-defined ring structures in their repeating units. Thus, a wide variety of polyacetals, polyesters, and polyamides having oxacycles in their main chains have been prepared by ring-opening polymerization of bicyclic acetals, oxalactones, and oxalactams.[1-3] Especially, polymers possessing six-membered tetrahydropyran rings are of practical importance, because the presence of tetrahydropyran rings often imparts desirable physical properties to the polymers including crystallinity, thermal stability, appropriate hydrophilicity, and excellent mechanical properties such as tenacity and modulus.

Among bicyclic oxalactams, ring-opening polymerization of 8-oxa-6-azabicyclo[3.2.1]octan-7-one (hereafter referred to as 8,6-BOL) has been most extensively investigated. It is readily polymerized anionically at room temperature to give amphiphilic polyamide **1** consisting of cis-2,6-linked tetrahydropyran rings.[4,5] The membranes of **1** and its block copolymers are characterized by excellent permeability for water and permselectivity for alkali-metal ions as well as solutes of various sizes in aqueous

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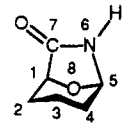
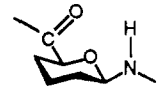


8, 6-BOL



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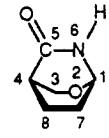
solution.[6-8] Of particular interest is a unique phenomenon that when aqueous solutions of some proteins were permeated through a porous membrane of an ABA block copolymer composed of 1 and polyethylene glycol as the A and B segments, respectively, the concentrations of permeated solutions became higher than those of the original solutions.[9]

As an extension of the studies on the ring-opening polymerization of heterobicyclic compounds and the synthesis of specialty polymers therefrom, 2-oxa-6-azabicyclo-[2.2.2]octan-5-one (2,6-BOL), a stereoisomer of 8,6-



2, 6-BOL

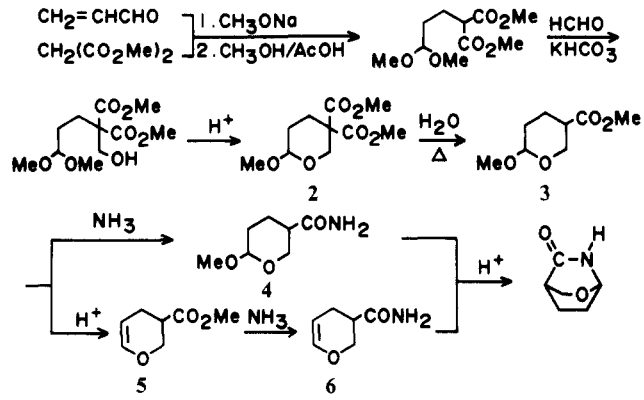
BOL, was newly synthesized and its ring-opening polymerizability was examined. The bicyclo[2.2.2]octane system occurs in the two-boat form. Its angle strain is generally small, but the system has H–H nonbonded interactions.[10] In fact, bicyclic ethers,[11,12] acetals,[13] orthoesters,[14-17] lactones,[18-21] and lactams[10,21] composed of this bicyclic skeleton are polymerizable. For example, 2-azabicyclo[2.2.2]octan-3-one undergoes ring-opening polymerization in the presence of sodium hydride to give polyamide containing trans-1,4-linked cyclohexane rings.[22]

The present paper describes the synthesis and ring-opening polymerization of 2,6-BOL and discusses the marked effect of the skeleton structure and the ether oxygen atom on the ring-opening polymerization behavior, in comparison with the polymerization of the related bicyclic lactam, 8,6-BOL.

Results and Discussion

Synthesis of Monomer. 2,6-BOL was synthesized starting from acrolein and dimethyl malonate through a six-step reaction sequence as illustrated in Scheme I. The synthesis of dimethyl 6-methoxytetrahydropyran-3,3-dicarboxylate (2) from the starting materials was described in a previous paper dealing with the synthesis and ring-opening polymerization of a bicyclic lactone possessing a bicyclo[2.2.2]octane skeleton.[19] The diester 2 was heated in dimethyl sulfoxide in the presence of small amounts of water and sodium chloride according to Krapcho's procedure for the one-step synthesis of monoesters from geminal diesters.[23,24] Methyl 6-methoxytetrahydropyran-3-carboxylate (3) was obtained as a mixture of the trans and cis forms. It was converted to the corresponding amide 4 by the treatment with aqueous ammonia. Finally the acid-catalyzed intramolecular bicyclization of 4 was achieved by heating it in a mixed solvent of dimethylformamide (DMF) and benzene (1:1, v/v) at 100–110 °C. The mixed solvent was used to avoid association of the amide in solution, which might cause intermolecular reaction leading to the formation of oligomeric substances. Under the conditions employed, the intramolecular bicyclization occurred to give the desired 2,6-BOL as a colorless solid after purification by successive column chro-

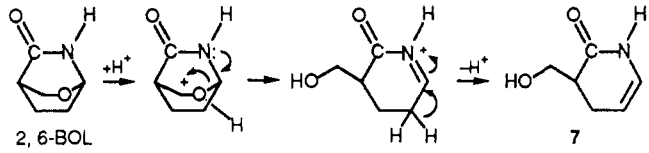
Scheme I
Synthetic Route for 2-Oxa-6-azabicyclo[2.2.2]octan-5-one (2,6-BOL)



matography, recrystallization from ethyl ether, and sublimation. The overall yield of 2,6-BOL based on acrolein was about 3%.

An alternative synthetic route involves the acid-catalyzed elimination of methanol from 3, the amidation of the resulting unsaturated ester 5, and the subsequent acid-catalyzed bicyclization of the unsaturated amide 6 in boiling acetonitrile. Compared with the bicyclization of 4 in a mixed solvent of DMF and benzene (1:1), the bicyclization of 6 in acetonitrile proceeded more rapidly to give 2,6-BOL. Although the yield was slightly lower, 2,6-BOL obtained by the reaction in acetonitrile was more easily purified.

In both of these methods, the intramolecular bicyclization was inevitably accompanied by the formation of a considerable amount of 3-(hydroxymethyl)-5,6-didehydro-2-piperidinone (7), along with an acetone-insoluble oli-



2, 6-BOL 7

gomeric substance. In fact, 2,6-BOL was found to be converted to 7 in the presence of a catalytic amount of *p*-toluenesulfonic acid in a mixed solvent of DMF and benzene (1:1) even at room temperature. Therefore, it appears that when 2,6-BOL is protonated on the ether oxygen atom, its C(1)–O(2) bond is readily cleaved due to the stereoelectronic effect of the amide nitrogen atom to give a monocyclic ion, from which deprotonation occurs to produce the unsaturated lactam 7.

2,6-BOL existed as hygroscopic crystals melting at 118.5–119.0 °C. Table I summarizes bond lengths and bond angles for 2,6-BOL determined by X-ray analysis.[25] Figure 1 presents a stereodrawing of this monomer. It is noteworthy that the C(1)–O(2) bond length of 2,6-BOL is 1.43 Å and the tetrahydropyran ring is nearly symmetrical. This is in sharp contrast to the shortening of the corresponding C(1)–O(6) bond (1.39 Å) and therefore unsymmetrical molecular dimension of the tetrahydropyran ring for 2,6-dioxabicyclo[2.2.2]octan-3-one (8), a

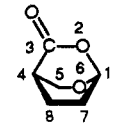


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Table I
Bond Lengths (Å) and Bond Angles (deg) for 2-Oxa-6-azabicyclo[2.2.2]octan-5-one (2,6-BOL)[a]

Bond Lengths			
O(2)–C(1)	1.430(2)	C(1)–C(7)	1.515(2)
O(2)–C(3)	1.440(2)	C(4)–C(5)	1.511(2)
O(9)–C(5)	1.235(2)	C(3)–C(4)	1.529(2)
N(6)–C(1)	1.452(2)	C(4)–C(8)	1.529(2)
N(6)–C(5)	1.336(2)	C(7)–C(8)	1.535(2)
Bond Angles			
C(1)–O(2)–C(3)	111.1 (1)	N(6)–C(5)–C(4)	109.9 (1)
C(1)–N(6)–C(5)	115.6 (1)	C(3)–C(4)–C(5)	107.6 (1)
O(2)–C(1)–N(6)	109.0 (1)	C(5)–C(4)–C(8)	108.0 (1)
O(2)–C(1)–C(7)	109.4 (1)	C(3)–C(4)–C(8)	107.6 (1)
N(6)–C(1)–C(7)	108.9 (1)	O(2)–C(3)–C(4)	110.1 (1)
O(9)–C(5)–N(6)	124.8 (1)	C(1)–C(7)–C(8)	107.9 (1)
O(9)–C(5)–C(4)	125.3 (1)	C(4)–C(8)–C(7)	108.3 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

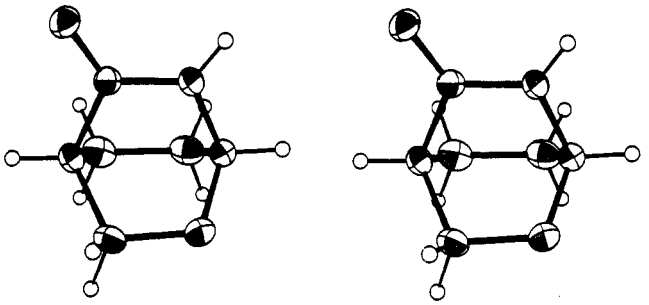

Figure 1. Stereodrawing of 2-oxa-6-azabicyclo[2.2.2]octan-5-one (2,6-BOL). The thermal ellipsoids are drawn at the 50% probability level.

bicyclic oxalactone having a similar skeleton.[19] The C(1)–O(6) bond of this bicyclic oxalactone is not cleaved at all in the cationic polymerization in accordance with Kirby's theoretical prediction.[26] On the contrary, the C(1)–O(2) bond of 2,6-BOL is readily cleaved, as reflected in the formation of the unsaturated lactam **7** in the final step of the monomer synthesis as described above. This finding suggests a possibility that 2,6-BOL undergoes cationic polymerization through the cleavage of the C(1)–O(2) bond under proper selection of reaction conditions. The bond angles C(4)–C(5)–N(6) and O(2)–C(1)–N(6) are 109.9° and 109.0°, respectively, which are considerably larger than the corresponding bond angles (104.8° and 101.3°) for 8,6-BOL.[27] This means that the angle strain of the lactam ring moiety of 2,6-BOL is considerably smaller than that of 8,6-BOL.

Anionic Polymerization. Anionic polymerization of 2,6-BOL was attempted in bulk at 120 °C or in dimethyl sulfoxide or THF at 30–60 °C. Potassium pyrrolidonate (KPyrdn) and *N*-benzoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one (BzBOL) were used as initiator and activator, respectively. The results are summarized in Table II.

In marked contrast to 8,6-BOL, 2,6-BOL did not give polyamide in anionic polymerization. Instead, it afforded a small amount of acetone-insoluble colorless solid whose major component was identified as a dimeric adduct **9**[28]

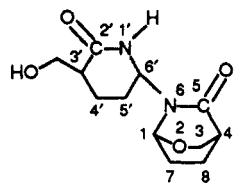

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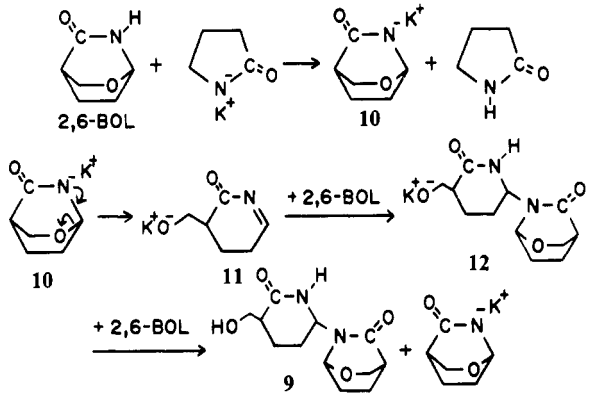
Table II
Attempted Anionic Polymerization of 2-Oxa-6-azabicyclo[2.2.2]octan-5-one

2,6-BOL, g	solvent[a] (mL)	KPyrdn,[b] mol %	activator,[c] mol %	temp, °C	time, h	yield,[d] %
0.45	none	3	2	120	0.5	85[e]
0.50	DMSO (1)	5	5	60	19	23
0.50	DMSO (2)	2	2	60	8	8
0.50	DMSO (2)	2	2	50	24	2
0.50	THF (4)	1	1	30–35	11[f]	24
0.50	DMSO (2)	1	1	30	24	0

[a] DMSO, dimethyl sulfoxide; THF, tetrahydrofuran. [b] Potassium pyrrolidonate. [c] *N*-Benzoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one. [d] Acetone-insoluble products. [e] Oligomers with complicated structures. [f] In days.

Scheme II
Mechanism for the Anionic Dimerization of 2-Oxa-6-azabicyclo[2.2.2]octan-5-one (2,6-BOL)



by spectroscopic analysis (^{1}H NMR, ^{13}C NMR, IR, and MS) along with elemental analysis. It is noteworthy that no benzoyl group was incorporated in the products. This is a clear indication that BzBOL did not participate in the reaction as an activator. The dimeric adduct **9** is presumably formed by the mechanism illustrated in Scheme II.

2,6-BOL reacts with KPyrdn to give the 2,6-BOL anion (**10**), as in the conventional anionic polymerization of other lactams including 8,6-BOL. However, as soon as the lactam anion **10** is formed, it must be selectively ring-opened at the C(1)–O(2) bond to form an alkoxide anion (**11**) before it attacks an activator molecule. The alkoxide anion (**11**) thus formed contains a reactive carbon–nitrogen double bond conjugated with a carbonyl group. Therefore, the nucleophilic addition of 2,6-BOL occurs on the reactive carbon atom to produce a dimer anion **12**. Abstraction of a proton from 2,6-BOL by the dimer anion **12** would yield the dimeric adduct **9** and regenerate the 2,6-BOL anion (**10**). However, the equilibrium of this step should lie far to **12** because the basicity of the dimer alkoxide anion **12** is lower than that of the 2,6-BOL anion (**10**). This is the reason why the yield of **9** was very low except in the polymerization carried out with a larger amount of the initiator and for a longer reaction time.

The lack of anionic polymerizability of 2,6-BOL must be ascribable to the instability of the 2,6-BOL anion (**10**). One of the lone-pair orbitals on the nitrogen atom of the 2,6-BOL anion is perfectly antiperiplanar to the C(1)–O(2) bond, which causes the facile cleavage of this bond (Figure 2). Thus, as soon as the 2,6-BOL anion is formed, it is transformed to the alkoxide anion (**11**), and, as a consequence, anionic polymerization by a so-called "activated monomer" mechanism does not take place. In contrast, neither of the lone-pair orbitals of the 8,6-BOL anion

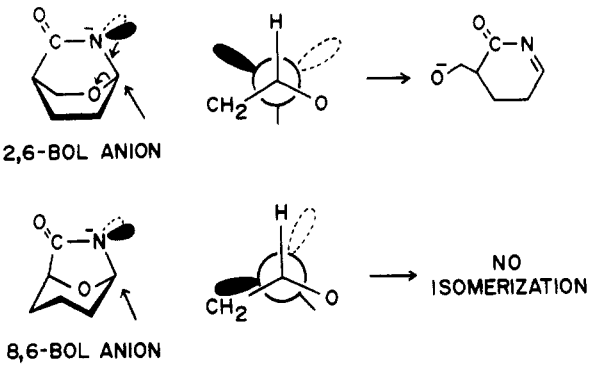


Figure 2. Stereoelectronic effect on the isomerization of bicyclic lactam anions.

is antiperiplanar to the C(5)–O(8) bond, and therefore the 8,6-BOL anion does not isomerize to an alkoxide anion corresponding to **11** (Figure 2).

Cationic Polymerization. Cationic polymerization of 2,6-BOL was carried out in dichloromethane or 1,1,1,3,3,3-hexafluoro-2-propanol at different temperatures ranging from −78 to +30 °C. Trifluoromethanesulfonic acid and bis[(trifluoromethyl)sulfonyl]methane were effective initiators. The latter is reportedly a stronger acid than trifluoroacetic acid and its estimated pK_a is about −1.[29] The reaction mixtures became heterogeneous in these solvents as the polymerization proceeded. The results are listed in Table III.

Although no polymerization occurred at or below −60 °C, 2,6-BOL underwent cationic polymerization relatively easily at or above −20 °C to yield colorless powdery products melting at 148–159 °C with decomposition. The products were soluble in *m*-cresol, 2,2,2-trifluoroethanol (TFE), and a mixture of TFE and chloroform (1:1, v/v). They decomposed in acidic solvents such as acetic acid and dichloroacetic acid. Vapor pressure osomometry in TFE showed that the number average molecular weights of the products were only several hundreds.

As shown in Scheme III, there are three possible ring-opening modes of 2,6-BOL in its cationic polymerization: (1) The C(5)–N(6) bond cleavage (a) would lead to polyamide composed of cis-2,5-linked tetrahydropyran rings. (2) The C(1)–N(6) bond cleavage (b) would give rise to polyamide consisting of trans-2,6-linked tetrahydropyran rings (S_N2) or a mixture of trans- and cis-2,6-linked tetrahydropyran rings (S_N1). (3) The C(1)–O(2) bond cleavage (c) would yield polyether composed of trans-3,6-linked 2-piperidinone rings (S_N2) or a mixture of cis- and trans-3,6-linked 2-piperidinone rings (S_N1).

A typical ^{13}C NMR spectrum of the oligomeric products is shown in Figure 3, along with the assignments (the chemical shift data are given in the Experimental Section). The chemical shifts were completely identical with those of poly(2-piperidinone-3,6-diyloxymethylene) obtained by the addition polymerization of the unsaturated lactam **7** in dichloromethane at 0 °C with trifluoromethanesulfonic acid as the initiator. The agreement means that the cationic polymerization of 2,6-BOL affords polyether containing six-membered lactam rings in the main chain, instead of polyamide containing tetrahydropyran rings; in other words, the selective cleavage of the C(1)–O(2) bond occurs in the cationic polymerization of 2,6-BOL. This is consistent with the unavoidable formation of the unsaturated lactam **7** in the final step of the synthesis of 2,6-BOL and the acid-catalyzed isomerization of 2,6-BOL to **7** as described above. At present, however, we cannot decide whether 2,6-BOL undergoes ring-opening polymerization or addition polymerization of the unsaturated lactam **7** generated from it in the cationic polymerization.

In Figure 3, each signal except the signals c and d appears as a pair of peaks of different intensities, indicating either that there are two types of structural units in the polymer chain or that the product is a mixture of two structurally similar compounds. Although the reaction products were only very slightly soluble in chloroform, gel permeation chromatography revealed that at least the dissolved part was a mixture of two oligomeric components differing in molecular weights.

The product obtained in hexafluoroisopropyl alcohol showed only a set of six sharp signals in its ^{13}C NMR spectrum and that there was only one peak corresponding to the lower molecular weight component in its gel permeation chromatogram. Moreover, mass spectroscopy by the fast atom bombardment technique indicated the presence of a weak molecular ion peak (M^+ + 1) at 509. These findings suggest that the lower molecular weight oligomer is most likely a cyclic tetramer. Although not clear at present, the precipitation of the product out of the solution must be a major factor for the highly selective formation of the oligomer of the specific size. The compositions of the oligomers approximately estimated by ^{13}C NMR spectroscopy are listed in Table I.

In relation to the aforementioned selective ether bond cleavage in the cationic polymerization of 2,6-BOL, Ogata et al.[31] proposed that some seven-membered lactam ethers underwent cationic polymerization at 100 °C or above through the selective cleavage of their ether bonds, on the basis of the fact that ε-caprolactam did not polymerize under similar conditions. The same authors also found that the attempted Beckmann rearrangement of the oxime of 9-oxabicyclo[3.3.1]nonan-3-one did not give the expected bicyclic lactam ether, 10-oxa-3-azabicyclo[4.3.1]decan-4-one, but a polymer.[32] On the basis of the IR spectroscopic analysis, they speculated that the polymer was produced by the ring-opening polymerization of the cyclic ether moiety of the once-formed bicyclic lactam ether in acidic media.

The cationic polymerization behavior of 2,6-BOL described above significantly differs from that of 8,6-BOL: The latter monomer gave a mixture of dimers and higher oligomers in the presence of cationic initiators such as trifluoromethanesulfonic acid and boron trifluoride etherate.[30] From the spectroscopic analysis of the isolated dimers from racemic and optically active 8,6-BOL, it was concluded that the cationic oligomerization involved the protonation onto the amide nitrogen of 8,6-BOL and the subsequent selective scission of the C(5)–N(6) bond, while the C(5)–O(8) bond was intact.

In summary, a newly prepared bicyclic oxalactam 2,6-BOL, unlike its structural isomer 8,6-BOL, did not polymerize anionically to high molecular weight polyamide, but it gave the dimeric adduct **9** in low yield under similar conditions where 8,6-BOL is readily polymerized to produce high molecular weight polyamide **1**. This is interpreted in terms of the rapid isomerization of the 2,6-BOL anion (**10**) to the alkoxide anion (**11**), assisted by the stereoelectronic effect. In contrast, 2,6-BOL was polymerized relatively easily with cationic initiator to afford polyether-type oligomers containing six-membered lactam rings via the selective C(1)–O(2) bond cleavage.

Experimental Section

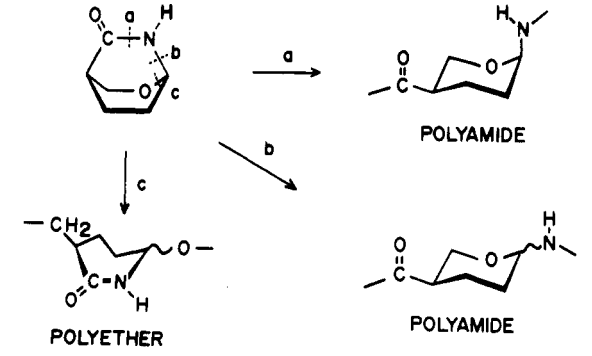
General Methods. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM FX-200 spectrometer operating at 200 (^1H)

Table III
Cationic Oligomerization of 2-Oxa-6-azabicyclo[2.2.2]octan-5-one

2,6-BOL, g	solvent[a] (mL)	initiator (mol %)	temp, °C	time, h	yield,[b] %	M_n[c]	H/L[d]
0.5	DM (2.0)	CF_3SO_3H (1.6)	0	3	76	630	37/63
0.3	DM (1.1)	CF_3SO_3H (5.0)	0	48	99	650	60/40
0.5	HFP (2.0)	CF_3SO_3H (1.1)	0	4	58	530	~0/~100
0.5	DM (2.0)	$(CF_3SO_2)_2CH_2$ (0.8)	0	20	69	650	47/53
0.5	DM (2.0)	CF_3SO_3H (2.0)	-20	22	58	640	45/55
0.5	NP (2.0)	$BF_3O(C_2H_5)_2$ (12.7)	-60	3	0		
0.5	DM (2.0)	CF_3SO_3H (2.0)	-78	4	0		

[a] DM, dichloromethane; HFP, 1,1,1,3,3,3-hexafluoro-2-propanol; NP, 1-nitropropane. [b] Acetone-insoluble products. [c] Number average molecular weight determined by vapor pressure osmometry in 2,2,2-trifluoroethanol. [d] Weight ratio of higher and lower oligomers estimated by ^{13}C NMR spectroscopy.

Scheme III
Possible Ring-Opening Modes of 2-Oxa-6-azabicyclo[2.2.2]octan-5-one (2,6-BOL) in Its Cationic Polymerization



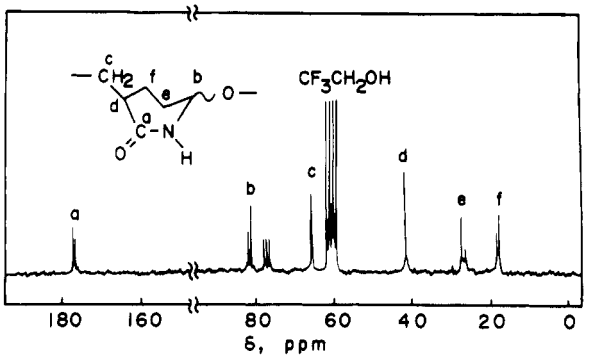


Figure 3. ^{13}C NMR spectrum of poly(2-piperidinone-3,6-diyloxymethylene). Solvent, $CF_3CH_2OH/CDCl_3$ (1:1, v/v); room temperature; TMS; 50 MHz.

and 50 MHz (^{13}C), respectively, on solutions in deuteriochloroform and dimethyl-d_6 sulfoxide. Tetramethylsilane was used as internal reference. IR spectra were taken on a Jasco A-3 spectrophotometer.

Preparation of Methyl 6-Methoxytetrahydropyran-3-carboxylate (3). Dimethyl 6-methoxytetrahydropyran-3,3-dicarboxylate[19] (2; 119.5 g, 0.52 mol) was heated at 150 °C for 10 h in dimethyl sulfoxide (500 mL) containing water (10.0 mL) and sodium chloride (5.0 g). After it was cooled to room temperature, the reaction mixture was poured into a large volume of water. The aqueous solution was extracted with diethyl ether three times. The combined extracts were dried over anhydrous sodium sulfate. After filtration, the solvent was removed by rotary evaporation and the oily residue was distilled under reduced pressure. The monoester 2 was obtained as a mixture of the cis and trans isomers (56:44 by ^1H NMR): yield 72.6 g (81%); bp 63 °C (1 mmHg). IR (neat): 1740 ($\nu_{C=O}$), 1125, 1055, 1025 (ν_{C-O-C}) cm^{-1}. ^1H NMR ($CDCl_3$): cis isomer, δ 4.62 (t, H-6), 3.98–3.78 (m, 2 H-2), 3.68 (s, CO_2CH_3), 3.36 (s, OCH_3), 2.75–2.44 (m, H-3), 2.12–1.48 (m, 2 H-4, 2 H-5); trans isomer, δ 4.49–4.43 (m, H-6), 4.17–4.01 (m, 2 H-2), 3.71 (s, CO_2CH_3), 3.42 (s, OCH_3), 2.73–2.44 (m, H-3), 2.12–1.48 (m, 2 H-4, 2 H-5). ^{13}C NMR ($CDCl_3$): cis isomer, δ 172.93 (C=O), 97.55 (C-6), 60.28 (C-2), 54.60 (OCH_3), 51.57 (CO_2CH_3), 40.41 (C-3), 28.91 (C-5), 21.15 (C-4); trans isomer, δ 173.10 (C=O), 100.39 (C-6), 63.07 (C-2), 55.38 (OCH_3), 51.66 (CO_2CH_3), 40.11 (C-3), 28.43 (C-5), 22.29 (C-4).

Preparation of 6-Methoxytetrahydropyran-3-carboxamide (4). Methyl 6-methoxytetrahydropyran-3-carboxylate (3; 23.5 g, 0.135 mol) was stirred in 33% aqueous ammonia (60 mL) at room temperature for 16 h. Removal of the solvent by rotary evaporation gave a colorless solid which was purified by recrystallization from benzene: yield 19.8 g (92%); mp 93.5–94.5 °C. IR (KBr): 3330, 3160 (ν_{N-H}), 1660 ($\nu_{C=O}$), 1625 (ν_{N-H}), 1110, 1050 (ν_{C-O-C}) cm^{-1}. ^1H NMR ($CDCl_3$): cis isomer, δ 5.95 (br, NH_2), 4.60 (t, H-6), 3.76–3.68 (m, 2 H-2), 3.38 (s, OCH_3), 2.55–2.40 (m, H-3), 2.27–1.76 (m, 2 H-4, 2 H-5); trans isomer, δ 6.32 (br, NH_2), 4.54 (dd, H-6), 4.10–4.02 (m, 2 H-2), 3.42 (s, OCH_3), 2.55–2.40 (m, H-3), 2.27–1.76 (m, 2 H-4, 2 H-5). ^{13}C NMR ($CDCl_3$): cis isomer, δ 175.27 (C=O), 98.24 (C-6), 61.16 (C-2), 54.91 (OCH_3), 42.14 (C-3), 28.81 (C-5), 22.28 (C-4); trans isomer, δ 175.88 (C=O), 99.89 (C-6), 62.63 (C-2), 55.50 (OCH_3), 41.17 (C-3), 27.96 (C-5), 22.69 (C-4).

Preparation of Methyl 3,4-Dihydro-2*H*-pyran-3-carboxylate (5). A solution of 3 (7.6 g, 0.044 mol) and *p*-toluenesulfonic acid monohydrate (100 mg, 0.53 mmol) in dry toluene (150 mL) was refluxed for 10 h in a flask equipped with a Soxhlet extractor containing 4A molecular sieves in a thimble. After the solution was cooled to room temperature, sodium carbonate (10 g) was added and the mixture was stirred for 30 min. The mixture was filtered, and the filtrate was distilled under reduced pressure to yield 5 as a transparent liquid: yield, 64%; bp 55 °C (5 mmHg). IR (neat): 1735 ($\nu_{C=O}$), 1650 ($\nu_{C=C}$), 1065 (ν_{C-O-C}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.37 (m, 1 H, H-6), 4.74 (m, 1 H, H-5), 4.22 (ddd, J = 1.4 Hz, J = 3.4 Hz, J = 10.6 Hz, 1 H, H-2_{eq}), 3.92 (dd, J = 9.2 Hz, J = 10.6 Hz, 1 H, H-2_{ax}), 3.72 (s, 3 H, OCH_3), 2.87 (m, 1 H, H-3), 2.2–2.4 (m, 2 H, 2 H-4). ^{13}C NMR ($CDCl_3$): δ 172.93 (C=O), 143.77 (C-6), 99.30 (C-5), 65.80 (C-2), 51.86 (CO_2CH_3), 38.66 (C-4), 22.70 (C-3).

Preparation of 3,4-Dihydro-2*H*-pyran-3-carboxamide (6). A heterogeneous mixture of 5 (8.0 g, 0.050 mol) and 33% aqueous ammonia (24 mL) was stirred at room temperature for 5 h. The mixture became a homogeneous solution as the reaction proceeded. The solution was salted out with excess sodium chloride and extracted with two 200-mL portions of chloroform. After filtration, the solvent was removed by rotary evaporation to give a colorless solid. It was recrystallized from a mixed solvent of *n*-hexane and acetone (1:1, v/v): yield, 81%; mp 114–115 °C. IR (KBr): 3375, 3200 (ν_{N-H}), 1660 ($\nu_{C=O}$), 1630 ($\nu_{C=C}$), 1060 (ν_{C-O-C}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.34 (m, 1 H, H-6), 5.9 (br, 2 H, NH_2), 4.72 (m, 1 H, H-5), 4.10 (dd, J = 3.3 Hz, J = 10.9 Hz, 1 H, H-2_{eq}), 3.90 (dd, J = 8.1 Hz, J = 10.9 Hz, 1 H, H-2_{ax}), 2.73 (m, 1 H, H-3), 2.30 (m, 2 H, H-4). ^{13}C NMR ($CDCl_3$): δ 174.97 (C=O), 143.62 (C-6), 99.46 (C-5), 66.18 (C-2), 39.42 (C-3), 23.14 (C-4).

Preparation of 2-Oxa-6-azabicyclo[2.2.2]octan-5-one (2,6-BOL). A mixture of 6-methoxytetrahydropyran-3-carboxamide (5.0 g, 0.031 mol) and *p*-toluenesulfonic acid (0.7 g, 3.7 mmol) in a mixed solvent of benzene and dimethylformamide (1:1, v/v; 500 mL) was heated at 110 °C for 4 h in a flask equipped with a Soxhlet extractor with a thimble charged with 4A molecular sieves. After the solution was cooled to room temperature, anhydrous potassium carbonate (5 g) was added to the solution, and the mixture was stirred at room temperature

for 30 min. After filtration, the mixture was subjected to rotary evaporation to afford a brown oil. It was dissolved in acetone to remove insoluble material. Subsequent removal of acetone from the solution gave a viscous yellow oil, which was chromatographed over a silica gel column (eluent, *n*-hexane:ethyl acetate = 2:1, v/v). The fractions containing 2,6-BOL were collected, and the removal of the solvents gave slightly brown wax: yield 0.92 g (23%). Recrystallization from diethyl ether three times followed by sublimation afforded colorless crystals, mp 118.5–119.0 °C. IR (KBr): 3200 (ν_{N-H}), 1680 ($\nu_{C=O}$), 1020 (ν_{C-O-C}) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.27 (br, 1 H, NH), 5.04 (m, 1 H, H-1), 3.94 (dd, 2 H, 2 H-3), 2.64 (br s, 1 H, H-4), 2.0–2.2 (m, 1 H, H-7_{eq}), 1.8–2.0 (m, 3 H, H-7_{ax}, 2 H-8). ^{13}C NMR ($CDCl_3$): δ 175.13 (C=O), 77.13 (C-1), 66.47 (C-3), 38.80 (C-4), 28.96 (C-7), 20.34 (C-8). MS: *m/e* 127, 99, 72. Anal. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.68; H, 7.21; N, 10.93. Crystallographic data: monoclinic; a = 5.747 (1), b = 17.519 (5), c = 6.032 (2) Å; β = 99.44 (2)°; D_{calcd} 1.40 g/cm^3; space group $P2_1/n$.

Column chromatographic separation of the reaction mixture gave 3-(hydroxymethyl)-5,6-didehydro-2-piperidinone as a slightly brown liquid, yield 1 g (25%). IR (neat): 3300 (ν_{O-H} and ν_{N-H}), 1680 ($\nu_{C=C}$), 1040 (ν_{C-O-C}), 720 (ν_{C-H}, *cis*-alkene) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.70 (br, 1 H, NH), 6.05 (dd, 1 H, H-6), 5.10 (m, 1 H, H-5), 4.40 (br, 1 H, OH), 3.78 (d, J = 5.9 Hz, 2 H, CH_2OH), 2.5–2.7 (m, 1 H, H-3), 2.2–2.4 (m, 2 H, 2 H-4); ^{13}C NMR ($CDCl_3$): δ 173.96 (C=O), 124.31 (C-5), 105.16 (C-4), 62.47 (CH_2OH), 41.57 (C-2), 22.66 (C-3). MS: *m/e* 127, 96, 80, 78, 68, 56.

Anionic Polymerization of 2-Oxa-6-azabicyclo[2.2.2]-octan-5-one (2,6-BOL). 2,6-BOL, *N*-benzoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one, dimethyl sulfoxide, and a solution of potassium pyrrolidonate in dimethyl sulfoxide were charged in this order to an ampule. The ampule was evacuated, sealed, and allowed to stand in a thermostated bath. After a small amount of acetic acid was added to terminate the polymerization, the reaction mixture was poured into acetone. Acetone-insoluble products were collected on a sintered-glass filter and dried under reduced pressure. Thin-layer chromatography disclosed the presence of at least two products. The major component was isolated by column chromatography (eluent, acetone:methanol = 6:1, v/v). Crystallization from acetone afforded colorless crystals, which were identified as *N*-[3′-(hydroxymethyl)-2′-piperidinon-6′-yl]-2-oxa-6-azabicyclo[2.2.2]octan-5-one (**9**), mp 236.5–237 °C. IR (KBr): 3350 (ν_{O-H}), 3250 (ν_{N-H}), 1680, 1670 ($\nu_{C=O}$) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.86 (dd, 1 H, H-1), 5.73 (br, 1 H, NH), 5.20 (t, 1 H, H-6′), 3.97 (d, 2 H, 2 H-3), 3.75 (d, J = 6.1 Hz, 2 H, CH_2OH), 2.72 (br s, 1 H, H-4), 2.53–2.45 (m, 1 H, H-3′), 2.3–1.5 (m, 9 H, OH, 2 H-7, 2 H-8, 2 H-4′, 2 H-5′). ^{13}C NMR (Me_2SO-d_6): δ 173.06 (C-5), 171.22 (C-1′), 76.48 (C-1), 66.63 (C-3), 61.82 (CH_2OH), 60.10 (C-5′), 43.20 (C-2′), 39.37 (C-4), 29.03 (C-4), 26.74 (C-3′), 22.21 (C-4′), 20.19 (C-8). MS: *m/e* 254, 149, 128, 110, 99. Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.52; H, 7.11; N, 10.98.

Cationic Polymerization of 2-Oxa-6-azabicyclo[2.2.2]-octan-5-one (2,6-BOL). 2,6-BOL and solvent were charged in a glass ampule equipped with a three-way stopcock. The resulting solution was frozen, and a solution of initiator in the same solvent was added through the stopcock by a syringe under a stream of nitrogen. The ampule was evacuated, sealed, and allowed to stand at a constant temperature. A small amount of pyridine was added to terminate the polymerization, and the heterogeneous reaction mixture was poured into a large volume of acetone. The acetone-insoluble powdery product was collected on a glass filter, washed with acetone, and dried under reduced pressure to a constant weight: mp: 148–159 °C dec. IR (KBr): 3300, 3230 (ν_{H-H}), 1665 ($\nu_{C=O}$), 1110 (ν_{C-O-C}) cm^{-1}. ^{13}C NMR (CF_3CH_2OH:$CDCl_3$ = 1 : 1, v/v): lower oligomer, δ 176.52 (C=O), 81.91 (C-6), 66.40 (CH_2OH), 42.92 (C-3), 28.45 (C-5), 19.18 (C-4); higher oligomer, δ 176.45 (C=O), 82.25 (C-6), 66.45 (CH_2OH), 42.97 (C-3), 27.60 (C-5), 19.48 (C-4).

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