Polymer Journal, Vol. 16, No. 11, pp 815—823 (1984)

Polymerization of Bicyclic Acetals XII. Synthesis and Polymerization of 4(*a*)-Benzyloxy-3(*e*)-cyano-6,8-dioxabicyclo[3.2.1]octane

Akira SUMI, Masahiko OKADA, and Hiroshi SUMITOMO

Faculty of Agriculture, Nagoya University, Chikusa, Nagoya 464, Japan

(Received March 27, 1984)

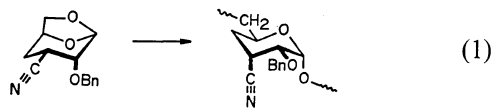
ABSTRACT: A new polysaccharide analogue (**2**) having regiospecifically a benzyloxy group and a cyano group in its repeating unit was synthesized by the cationic ring-opening polymerization of 4(*a*)-benzyloxy-3(*e*)-cyano-6,8-dioxabicyclo[3.2.1]octane (**1**). The bicyclic acetal **1** was prepared from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer) *via* six reaction steps. The ring-opening polymerization of **1** proceeded, though very slowly, in dichloromethane at temperatures between −60 and 0°C in the presence of strong Lewis acids such as antimony pentafluoride and antimony pentachloride as initiators, yielding polyacetals (poly(3(*e*)-benzyloxy-4(*a*)-cyanotetrahydropyran-6,2-diyloxymethylene)) with number average molecular weights of $\sim 1.4 \times 10^4$. ^{1}H and ^{13}C NMR analysis disclosed that polymer **2** consisted exclusively of tetrahydropyranoside units linked in a (1→6)-α fashion according to carbohydrate chemistry terminology. On heating the polymer **2** with potassium hydroxide in an aqueous 2-methoxyethanol solution, inversion of the configuration of the carbon atom bearing the cyano group occurred to give a structural unit having the cyano group in the equatorial position. The polymerization reactivity of **1** was markedly lower than those of analogous bicyclic acetals. The retarding effect of the cyano group on the polymerization of **1** is discussed.

KEY WORDS Ring-Opening Polymerization / Cationic Polymerization / Bicyclic Acetal / 6,8-Dioxabicyclo[3.2.1]octane Derivative / Cyano Group /

Chemical synthesis of polysaccharides, especially those displaying biological and physiological activity, is of considerable interest to synthetic polymer chemists. In recent years, a variety of polysaccharides have been synthesized, mostly by the ring-opening polymerization of anhydrosugars and their related compounds.[1-6] However, the number of publications dealing with the chemical synthesis of polysaccharides having physiologically and pharmaceutically important functional groups such as amino, carboxyl, sulfate, and sulfoamino groups is very limited. For example, we previously synthesized some sulfated DL-polysaccharides of a dextran type by the controlled ring-opening polymerization of an unsaturated bicyclic acetal, 6,8-dioxabicyclo-[3.2.1]oct-3-ene, followed by appropriate chemical modifications of the resulting polymer having a dihydropyran ring in its repeating unit, and evaluated their anticoagulant activities.[7,8] More recently, Uryu *et al.*[9] obtained an aminated polysaccharide by the ring-opening polymerization of 1,6-anhydro-3-azido-2,4-di-*O*-benzyl-3-deoxy-β-D-glucopyranose and the subsequent lithium aluminum hydride reduction of azido groups in the resulting polymer followed by debenzylation.

As an approach to the molecular design of structurally well-defined polysaccharides with physiological activities, we undertook the synthesis of 4(*a*)-benzyloxy-3(*e*)-cyano-6,8-dioxabicyclo[3.2.1]octane (**1**), a hitherto unknown bicyclic acetal, from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer) and its

ring-opening polymerization to a polysaccharide analogue (**2**). Polymer **2** contains regiospecifically a benzyloxy group and a cyano group in its repeating unit, which can be chemically transformed under suitable reaction conditions to physiologically important functional groups. The present article describes the synthesis and ring-opening polymerization of bicyclic monomer **1** with emphasis on the stereochemical aspects involved therein.



(1)

1 **2** Bn, $-CH_2C_6H_5$

EXPERIMENTAL

4(*a*)-Benzyloxy-3(*e*)-cyano-6,8-dioxabicyclo[3.2.1]octane (**1**) was synthesized from 3,4-dihydro-2*H*-pyran-2-carbaldehyde *via* the six reaction steps illustrated in Scheme I: 3,8,9-Trioxatricyclo[4.2.1.$0^{2,4}$]nonane (**7**) was prepared from **1** by sodium borohydride reduction, bromination accompanied by cyclization, dehydrobromination, and subsequent epoxidation according to the procedures described by Brown *et al.*[10,11] with some modifications.

*Preparation of 3(e)-Cyano-4(a)-hydroxy-6,8-dioxabicyclo[3.2.1]octane (**8**)*

The reaction of **7** with potassium cyanide was carried out in an aqueous solution buffered by magnesium sulfate as described for the preparation of 3-hydroxyglutaronitrile from epichlorohydrin and potassium cyanide.[12] A saturated aqueous solution of magnesium sulfate (60 ml) and potassium cyanide (6.0 g, 0.09 mol) were placed in a three-necked flask with a reflux condenser and dropping funnel, and the solution was stirred at room temperature. After the solution became turbid due to precipitation of magnesium hydroxide, **7** (3.9 g, 0.03 mol) was added through the dropping funnel, and the mixture was heated for 5 h at 85°C with vigorous mechanical stirring. The reaction mixture was cooled to room temperature, and the precipitate in the reaction mixture was filtered off. The filtrate was extracted with seven 100 ml portions of ethyl acetate, and the combined extract was dried over anhydrous magnesium sulfate. The drying agent was filtered, and the solvent was removed with a rotary evaporator to give a viscous oil (3.3 g). This was recrystallized from ethanol at least twice to afford white crystals (2.5 g, 54%); mp 87.5—88.5°C. *Anal.* Calcd for $C_7H_9NO_3$: C, 54.19%; H, 5.85%; N, 9.03%. Found: C, 54.02%; H, 5.86%; N, 9.06%.

*Preparation of 4(a)-Benzyloxy-3(e)-cyano-6,8-dioxabicyclo[3.2.1]octane (**1**)*

Benzylation of **8** was carried out according to the procedure described for the preparation of 1,6-anhydro-2,4-di-*O*-benzyl-β-D-glucopyranose from 1,6-anhydro-β-D-glucopyranose.[13] The hydroxyl compound **8** (2.16 g, 0.014 mol), finely pulverized barium oxide (2.18 g, 0.014 mol), and dry dimethylformamide (55 ml) were placed in a three-necked flask equipped with a reflux condenser and a dropping funnel, and the mixture was stirred under a stream of dry nitrogen. Benzyl bromide (1.65 ml, 0.0139 mol) was added dropwise to the solution at room temperature, and the reaction mixture was heated in an oil bath preheated at 60°C. Consumption of **8** was monitored by thin layer chromatography. When it was consumed (reaction time 60—80 min), the reaction mixture was cooled quickly to room temperature. Methanol (28 ml), water (55 ml), and 1% aqueous hydrochloric acid (55 ml) were dropped successively into the mixture. The resulting solution was extracted with six 100 ml portions of chloroform. The chloroform extract was washed with water (200 ml) three times and dried over anhydrous magnesium sulfate overnight. After the filtration of the drying reagent, the solvent was removed by rotary

evaporation to give an amber residue. It was recrystallized at least four times to afford **1** as white needles (1.1 g, 31%); mp 110.5—111.5°C. *Anal.* Calcd for $C_{14}H_{15}NO_3$: C, 68.56%; H, 6.16%; N, 5.71%. Found: C, 68.33%; H, 6.14%; N, 5.64%.

*Polymerization of 4(a)-Benzyloxy-3(e)-cyano-6,8-dioxabicyclo[3.2.1]octane (**1**)*

Prior to polymerization, monomer **1** was purified by repeated recrystallization from ethanol and subsequently from a mixed solvent of dichloromethane and *n*-hexane (1 : 2 by vol). Dichloromethane and chloroform had been refluxed over calcium hydride for several days and fractionally distilled just before use. Antimony pentachloride and trifluoromethanesulfonic acid were purified by distillation under reduced pressure, while antimony pentafluoride was used as supplied. Phosphorus pentafluoride was generated by the thermal decomposition of *p*-chlorobenzenediazonium hexafluorophosphate. Monomer **1** was charged into an ampule and thoroughly dried under vacuum for several days. Then solvent was added into the ampule to dissolve **1**, and the solution was frozen in a liquid nitrogen bath. A specified amount of initiator dissolved in the same solvent was added to the ampule. The addition of the solvent and the initiator was carried out under a dry nitrogen atmosphere to minimize the contamination of moisture. The ampule was evacuated, sealed off, and allowed to stand in a bath kept at constant temperature. When phosphorus pentafluoride was used as an initiator, a high vacuum technique was employed for the polymerization. The polymerization was terminated by the addition of a small amount of pyridine, and the mixture was poured into a large excess of methanol to precipitate a polymer. The polymer was purified by repeated reprecipitation using dichloromethane and methanol as a solvent–precipitant pair, followed by freeze-drying from a benzene solution.

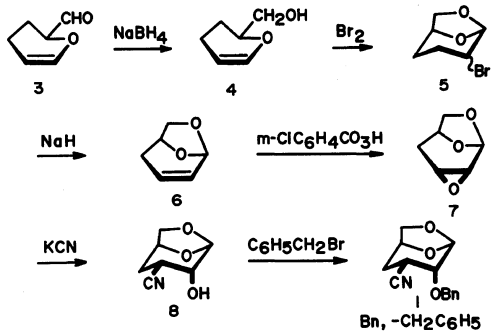
Characterization

^1H and ^{13}C NMR spectra were recorded at room temperature or 50°C on a JNM FX-200 Fourier transform spectrometer operating at 200 and 50 MHz, respectively. Deuteriochloroform and tetramethylsilane were employed as the solvent and internal reference. Number average molecular weights of the polymers were estimated by a Hitachi 634A gel permeation chromatograph (column, Shodex A80M, 1 m; eluent, chloroform; polystyrene standard).

RESULTS AND DISCUSSION

*Synthesis of 4(a)-Benzyloxy-3(e)-cyano-6,8-dioxabicyclo[3.2.1]octane (**1**)*

Bicyclic acetal **1** was synthesized from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer, **3**) *via* the six reaction steps illustrated in Scheme I. The sodium borohydride reduction of **3** and subsequent bromination accompanied by cyclization gave a stereoisomer mixture of 4(*a*)- and 4(*e*)-bromo-6,8-dioxabicyclo[3.2.1]-octane (**5**). The dehydrobromination of the mixture with sodium hydride in 1,2-dimethoxyethane afforded 6,8-dioxabicyclo-[3.2.1]oct-3-ene (**6**) together with the unreacted 4(*e*)-bromo-6,8-dioxabicyclo[3.2.1]-octane which were readily separated by distillation. Olefin **6** was oxidized with *m*-chloroperbenzoic acid to yield 3,8,9-trioxatricyclo-



Scheme I. Synthetic route of 4(*a*)-benzyloxy-3(*e*)-cyano-6,8-dioxabicyclo[3.2.1]octane (**1**).

[4.2.1.$0^{2,4}$]nonane (**7**). All these reactions were carried out according to the procedures described by Brown *et al.*[10,11] with some modifications.

Tricyclic compound **7** was heated with potassium cyanide in a saturated aqueous solution of magnesium sulfate to give 3(*e*)-cyano-4(*a*)-hydroxy-6,8-dioxabicyclo[3.2.1]octane (**8**). Since nucleophilic additions onto epoxides are generally accompanied by *trans* ring-opening, the reaction of **7** with potassium cyanide was expected to produce 3(*a*)-cyano-4(*a*)-hydroxy-6,8-dioxabicyclo[3.2.1]octane. But actually, ^{1}H NMR analysis showed the product to be 3(*e*)-cyano-4(*a*)-hydroxy-6,8-dioxabicyclo[3.2.1]octane (**8**).

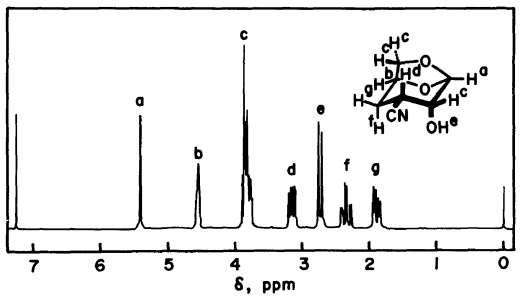
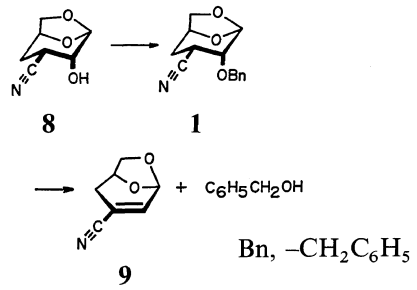


Figure 1. ^{1}H NMR spectrum of 3(*e*)-cyano-4(*a*)-hydroxy-6,8-dioxabicyclo[3.2.1]octane (**8**): solvent, $CDCl_3$; concn, 2%; temp, 22°C; 200 MHz; internal reference, Me_4Si.

Figure 1 presents the ^{1}H NMR spectrum of **8** along with the assignments of the signals determined by the spin-decoupling method. The coupling constant between the protons d and f was found to be 12 Hz, which was close to the corresponding coupling constant ($J_{H_a(2)-H_a(3)} = 10$ Hz) for 3(*e*),4(*a*)-dihydroxy-6,8-dioxabicyclo[3.2.1]octane derived from **6** by osmium tetroxide oxidation.[14] This finding definitely shows the cyano group on the C(3) atoms to occupy the equatorial position. The abnormal stereochemistry in the reaction of the oxirane ring of **7** can be interpreted by a mechanism involving the abstraction of the methine proton adjacent to the cyano group. Thus, the nucleophilic attack of a cyanide ion occurs regioselectively on the C(3) atom of **7** for steric and electronic reasons[15] to give rise to a *trans* diaxially substituted compound. However, the methine proton on the carbon bearing the cyano group is readily abstracted under basic conditions to form a carbanion which isomerizes to an energetically more favorable form possessing the cyano group in the equatorial position, followed by reprotonation to give **8**.

The benzylation of **8** with benzyl bromide was achieved in the presence of barium oxide in dimethylformamide at 60°C. It should be noted here that the reaction for a prolonged time or at a higher temperature causes the elimination of benzyl alcohol from the desired product **1** to yield 3-cyano-6,8-dioxabicyclo-[3.2.1]oct-2-ene (**9**) as shown in eq 2. The side reaction is induced by abstraction of the labile methine proton neighboring the cyano group of **1** and the subsequent elimination of the benzyloxy group located in the anti position to the abstracted methine proton.



8 **1** **9** (2)

Polymerization of 4(a)-Benzyloxy-3(e)-cyano-6,8-dioxabicyclo[3.2.1]octane (1)

Some of the results of the polymerization of **1** are summarized in Table I. Monomer **1** underwent polymerization, although sluggishly, in the presence of strong Lewis acids such as antimony pentachloride and antimony pentafluoride in dichloromethane, but it did not polymerize in chloroform. Phosphorus pentafluoride and trifluoromethanesulfonic acid were ineffective in initiating the polymerization of **1**. It is to be noted that the polymerization reactivity of **1** is markedly lower than

Table I. Cationic polymerization of 4(*a*)-benzyloxy-3(*e*)-cyano-6,8-dioxabicyclo[3.2.1]octane (**1**)[a]

Initiator[b]	CH_2Cl_2	Temp	Time	Polymer[c]	M_n[d] $\times 10^{-3}$	α-Form[e]	mp
	ml	°C	day	%		%	°C
$SbCl_5$	1.9	0	3	1	—	—	96—110
$SbCl_5$	2.4	−40	3	5	6.7	~100	123—130
$SbCl_5$	3.5	−60	3	9	9.6	~100	120—135
$SbCl_5$	3.5	−60	5	16[g]	10.6	~100	119—125
SbF_5	3.5	−60	5	27	8.2	~100	129—132
SbF_5	2.0[f]	−60	1	0	—	—	—
PF_5	4.0	−60	11	0	—	—	—
CF_3SO_3H	3.5	−60	5	0	—	—	—

[a] Monomer, 0.49 g (2 mmol).
[b] 5 mol% to monomer.
[c] Methanol insoluble polymer. Besides methanol-insoluble polymer, methanol-soluble oligomeric materials were obtained in 2—5% yields in several runs. The rest was the unreacted monomer.
[d] By gel permeation chromatography.
[e] By ^{13}C NMR spectroscopy.
[f] Chloroform.
[g] *Anal.* Calcd for $(C_{14}H_{15}NO_3)_n$: C, 68.56%; H, 6.16%; N, 5.71%. Found: C, 68.57%; H, 6.16%; N, 5.44%.

that of the analogues of **1**, such as 6,8-dioxabicyclo[3.2.1]octane,[16] and its 4(*e*)-bromo-,[17] 4(*a*)-benzyloxy-,[18] 4(*e*)-benzyloxy-,[19] and 3(*a*),4(*a*)-bis(benzyloxy)[20] derivatives.

The polymers obtained were white powdery materials with number average molecular weights of $\sim 1.4 \times 10^4$. They were soluble in a variety of solvents including benzene, chloroform, tetrahydrofuran, ethyl acetate, and dimethylformamide, and insoluble in ethyl ether, acetone, *n*-hexane, and toluene.

The ^1H and ^{13}C NMR spectra of the polymer prepared at −60°C with antimony pentachloride as the initiator are presented in Figures 2 and 3, respectively. The assignments of the signals are given in the figures. It is clear from these spectra that the polymer consists exclusively of the tetrahydropyranoside units linked in the (1→6)-α fashion. (The (1→6)-α linked tetrahydropyranoside unit refers to the structural unit in which the exocyclic oxygen atom is oriented axially to the tetrahydropyran ring as illustrated in eq 1.) It is noteworthy that the peaks f, g, i, j, and k in the ^{13}C NMR spectrum (Figure 3) are somewhat broad

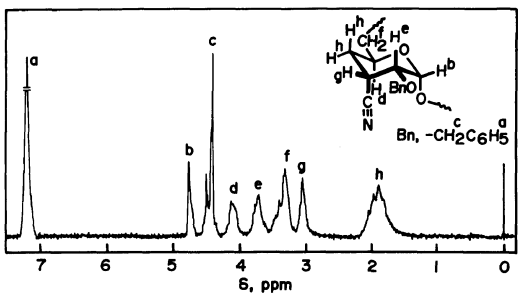


Figure 2. ^1H NMR spectrum of poly(3(*e*)-benzyloxy-4(*a*)-cyanotetrahydropyran-6,2-diyloxymethylene) (**2**) prepared with antimony pentachloride in dichloromethane at −60°C: Solvent, $CDCl_3$; temp, 50°C; 200 MHz; internal reference, Me_4Si.

owing to overlapping of the split signals with slightly different chemical shifts. As monomer **1** is racemic, the appearance of these split signals is probably ascribable to the different diad placements of the D- and L-enantiomeric monomeric units in the polymer chain. Similar but more distinct splittings of the signals were observed in the ^{13}C NMR spectra of the polymers of racemic 6,8-dioxabicyclo[3.2.1]-octane[16] and its 4(*e*)-bromo derivative,[17] and were confirmed to arise from the diad tacticities by comparing their ^{13}C NMR spectra

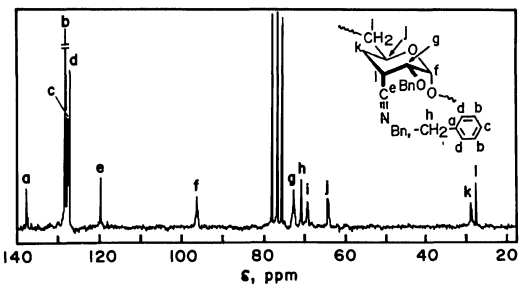


Figure 3. ^{13}C NMR spectrum of poly(3(*e*)-benzyloxy-4(*a*)-cyanotetrahydropyran-6,2-diyloxymethylene) (**2**) prepared with antimony pentachloride in dichloromethane at −60°C: Solvent, $CDCl_3$; temp, 50°C; 25 MHz; internal reference, Me_4Si.

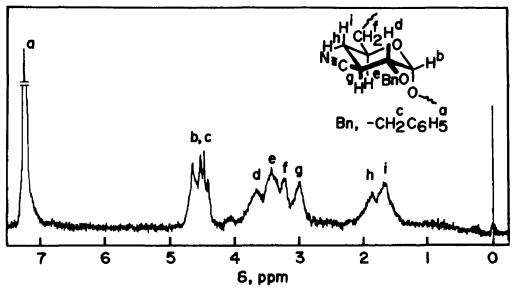


Figure 4. ^1H NMR spectrum of the polymer obtained by heating poly(3(*e*)-benzyloxy-4(*a*)-cyanotetrahydropyran-6,2-diyloxymethylene) (**2**) with potassium hydroxide in 2-methoxyethanol: Solvent, $CDCl_3$; temp, 50°C; 200 MHz; internal reference, Me_4Si.

with those of the corresponding optically active polymers.[21,22]

Under the reaction conditions of the cationic polymerization, the absolute configuration of the carbon bearing the cyano group is not altered. Since the ring-opening polymerization of **1** is accompanied by flipping of the tetrahydropyran ring, the cyano group is axially oriented to the tetrahydropyran ring in polymer **2**. (The IUPAC nomenclature is therefore poly(3(*e*)-benzyloxy-4(*a*)-cyanotetrahydropyran-6,2-diyloxymethylene).)

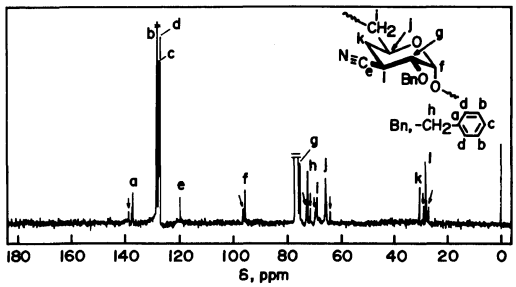
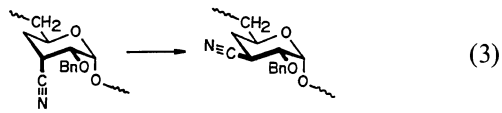


Figure 5. ^{13}C NMR spectrum of the polymer obtained by heating poly(3(*e*)-benzyloxy-4(*a*)-cyanotetrahydropyran-6,2-diyloxymethylene) (**2**) with potassium hydroxide in 2-methoxyethanol: Solvent, $CDCl_3$; temp, 50°C; 50 MHz; internal reference, Me_4Si.



(3)

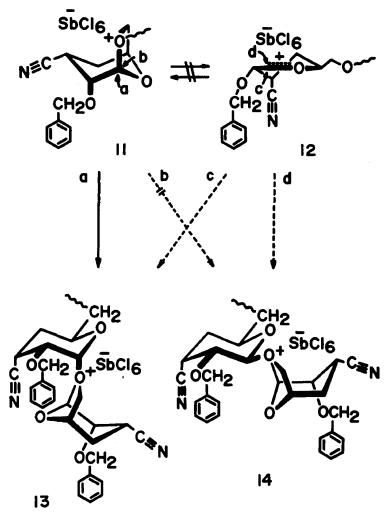
2 **10** Bn, $-CH_2C_6H_5$

When the polymer was heated with potassium hydroxide in a mixture of 2-methoxyethanol and water (50 : 8 by vol.) at 80°C for 24 h, many of the structural units in the origianl polymer isomerized to the energetically more stable structural units (**10**) having the equatorially oriented cyano group (eq 3). The ^1H and ^{13}C NMR spectra of the reaction product are shown in Figures 4 and 5, respectively.

In the ^1H NMR spectrum, the following two points are noticeable in comparison with the ^1H NMR spectrum of the original polymer (Figure 2). First, the methine proton signal on the C(6) atom of the isomerization product (peak e in figure 4) appears in a higher magnetic field than the corresponding signal of the original polymer (peak d in Figure 2). This is reasonably accounted for by the equatorial orientation of the cyano group in the former; that is, the diamagnetic anisotropic effect on the methine proton, if any, is negligibly small, while it should cause an appreciable downfield shift when the cyano group occupies the axial position. Secondly, the axial proton signal of the methylene group of the tetrahydropyran ring in the isomerization product (peak i in Figure 4) appears in a magnetic field higher than that for the original polymer (peak h in Figure 2). The up-field shift of the former is also consistent with the equatorial orieinta-

tion of the cyano group, whose diamagneic anisotropic effect shields the axial proton of the methylene group.

The weak signals marked with arrows in the ^{13}C NMR spectrum (Figure 5) are ascribable to the respective carbons of the unchanged structural units. The signal assignable to the C(6) atom in the spectrum of the isomerized structural unit appears at about 1.7 ppm downfield in comparison with that for the original structural unit. This is reasonably explained by the relief of the 1,3-steric compression effect resulting from the transfer of the cyano group from the axial position to the equatorial position. All these spectral data clearly show the cyano groups in the polymer to be originally located in axial positions and many of them to be transferred to the energetically favorable equatorial positions under the basic conditions employed.



Scheme II. Propagation processes in the polymerization of 4(*a*)-benzyloxy-3(*e*)-cyano-6,8-dioxabicyclo-[3.2.1]octane (**1**).

In the cationic ring-opening polymerization of bicyclic acetals possessing the same ring skeleton as that of **2**, some monomers tend to give, particularly at higher temperatures, polyacetals containing not only the tetrahydropyranoside units of the (1→6)-α type but also those of the (1→6)-β type, although the fraction of the latter is generally low. (The tetrahydropyranoside unit of the (1→6)-β type refers to the monomeric unit in which the exocyclic oxygen atom occupies the equatorial position of the tetrahydropyran ring.) The coexistence of both structural units in a polymer chain has been interpreted by the participation of the propagation by an oxacarbenium ion, in addition to the propagation by an trialkyloxonium ion.[23,24]

The polymers obtained at or below −30°C in the polymerization of **1** were composed exclusively of the (1→6)-α type structural unit. Therefore, the formation of the polyacetal with the regular (1→6)-α structural unit indicates that monomer **1** polymerizes by an S_N2 mechanism involving a backside attack of the monomer to the partially positively charged acetal carbon of the trialkyloxonium ion (**11**) (arrow a in Scheme II). In other words, the trialkyloxonium ion is relatively stable even at −30°C, so that it does not undergo unimolecular ring-opening to the oxacarbenium ion (**12**) before the addition of the monomer.

The reactivity of **2** in the cationic ring-opening polymerization, as described above, is markedly lower than those of analogous bicyclic acetals having a 6,8-dioxabicyclo-[3.2.1]octane skeleton. A dominant factor reducing the polymerization reactivity of **1** is conceivably the complexation between the cyano group of the monomer and Lewis acid initiators. It decreases the amount of the effective initiator which can participate in the initiation reaction. In this connection, it should be noted that an attempt to copolymerize an equimolar mixture of **1** and 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose with phosphorus pentafluoride as the initiator gave neither a copolymer nor homopolymer, although the latter monomer readily polymerizes in the absence of **1**. Such an inhibitory effect of **1** is presumably ascribable to the complexation between the cyano

group of **1** and phosphorus pentafluoride. The complexation between nitriles and Lewis acids has been verified spectroscopically, as for instance, in acetonitrile–tin tetrachloride[25,26] and acetonitrile–antimony pentachloride[27] systems as well as acrylonitrile–tin tetrachloride[28,29] and acrylonitrile–zinc chloride[30] systems.

Electronic repulsion between the equatorially oriented cyano and axially oriented benzyloxy groups in the active terminal unit might be responsible to some extent for the reduced reactivity of **1**. There occurs a repulsive interaction between the cyano group with a high electron density and the neighboring electron-rich benzyloxy group, so that they are forced apart from each other as much as possible. Consequently, the benzyloxy group is somewhat bent over the partially positively charged acetal carbon, thus preventing the approach of the monomer to the active center. In addition, when trialkyloxonium ion **11** is ring-opened with concomitant flipping of the tetrahydropyran ring by the attack of monomer **1**, the cyano and benzyloxy groups must pass through the eclipsed state. The electronic repulsion between these electron-rich groups makes this process energetically unfavorable compared with the corresponding reaction for the monomers without such a repulsive interaction, and therefore depresses the rate of the ring-opening polymerization of **1**.

In summary, 4(*a*)-benzyloxy-3(*e*)-cyano-6,8-dioxabicyclo[3.2.1]octane (**1**) was synthesized starting from acrolein dimer through six reaction steps. Monomer **1** underwent a sluggish, ring-opening polymerization in the presence of strong Lewis acids at low temperatures to give polysaccharide analogue **2** having regiospecifically a benzyloxy group and a cyano group in its repeating tetrahydropyranoside unit regularly linked in the (1→6)-α fashion. Since these two groups are chemically convertible to a variety of functional groups under appropriate reaction conditions, the polymer may be useful as a precursor for synthetic polysaccharides of potential physiological and pharmaceutical activity.

Acknowledgment. This research is one of a series of works of the Japan–U.S. Cooperative Science Program supported by the Japan Society for the Promotion of Science and the National Science Foundation of the U.S.A. We extend our sincere gratitude to Professor H. K. Hall, Jr. of the University of Arizona for his valuable comments and suggestions during the course of this work.

REFERENCES

1. I. J. Goldstein and T. L. Huller, *Adv. Carbohydr. Chem.*, **21**, 431 (1966).
2. C. Schuerch, *Adv. Polym. Sci.*, **10**, 173 (1972).
3. C. Schuerch, *Acc. Chem. Res.*, **6**, 184 (1973).
4. H. Sumitomo and M. Okada, *Adv. Polym. Sci.*, **28**, 47 (1978).
5. C. Schuerch, *Adv. Carbohydr. Chem. Biochem.*, **39**, 157 (1981).
6. H. Sumitomo and M. Okada, "Ring-Opening Polymerization I," K. Ivin and T. Saegusa, Eds., Applied Science Publishers, London, 1984, p 299.
7. M. Okada, H. Sumitomo, H. Hasegawa, and H. Komada, *Makromol. Chem.*, **180**, 813 (1979).
8. H. Komada, M. Okada, and H. Sumitomo, *Makromol. Chem.*, **181**, 2305 (1980).
9. T. Uryu, K. Hatanaka, K. Matsuzaki, and H. Kuzuhara, *Macromolecules*, **16**, 853 (1983).
10. F. Sweet and R. K. Brown, *Can. J. Chem.*, **46**, 2289 (1968).
11. R. M. Srivastava and R. K. Brown, *Can. J. Chem.*, **48**, 830 (1970).
12. F. Johnson, J. P. Panella, and A. A. Carlson, *J. Org. Chem.*, **27**, 2241 (1962).
13. T. Iversen and D. R. Bundle, *Can. J. Chem.*, **60**, 299 (1982).
14. T. P. Murray, U. P. Singh, and R. K. Brown, *Can. J. Chem.*, **49**, 2132 (1971).
15. J. Halbycy, T. Trnka, and M. Černý, *Collect. Czech. Chem. Commun.*, **38**, 2151 (1975).
16. M. Okada, H. Sumitomo, and H. Komada, *Macromolecules*, **12**, 395 (1979).
17. M. Okada, H. Sumitomo, and A. Sumi, *Macromolecules*, **15**, 1238 (1982).
18. M. Okada, H. Sumitomo, and K. Ogasawara, *Polym. J.*, **14**, 815 (1982).
19. M. Okada, H. Sumitomo, and K. Ogasawara, *Polym. J.*, **15**, 821 (1983).

20. M. Okada, H. Sumitomo, and Y. Hishida, *Makromol. Chem.*, **184**, 1823 (1983).
21. H. Komada, M. Okada, and H. Sumitomo, *Macromolecules*, **12**, 5 (1979).
22. M. Okada, H. Sumitomo, and A. Sumi, *Polym. Bull.*, **7**, 431 (1982).
23. J. Zachoval and C. Schuerch, *J. Am. Chem. Soc.*, **91**, 1165 (1969).
24. M. Okada, H. Sumitomo, and Y. Hibino, *Polym. J.*, **6**, 256 (1974).
25. I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J. Chem. Soc.*, 1514 (1963).
26. I. R. Biettie and L. Rule, *J. Chem. Soc.*, 3267 (1964).
27. I. R. Biettie and M. Webster, *J. Chem. Soc.*, 38 (1963).
28. H. Hirai, T. Ikegami, and S. Makishima, *J. Polym. Sci., A-1*, **7**, 2059 (1969).
29. B. Yamada, Y. Kusuki, and T. Otsu, *Makromol. Chem.*, **29**, 137 (1970).
30. T. Ikegami and H. Hirai, *J. Polym. Sci., A-1*, **8**, 195 (1970).