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Polymerization of Bicyclic Acetals XVI. Substituent Effect of an Equatorially Oriented Benzyloxy Group in Position 3 on the Stereochemical Course of the Cationic Ring-Opening Polymerization of 6,8-Dioxabicyclo-[3.2.1]octane Derivatives

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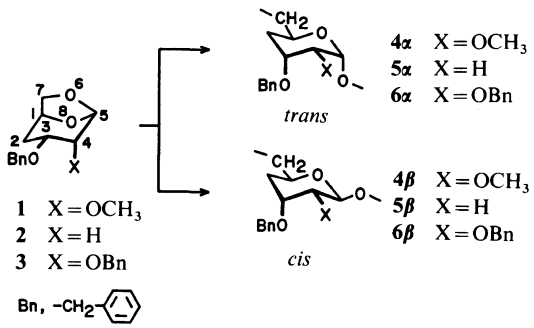
ABSTRACT: Ring-opening polymerization of 6,8-dioxabicyclo[3.2.1]octane derivatives possessing, as a common substituent, an equatorial benzyloxy group in position 3 was investigated to clarify an important role of the substituent in the formation of structurally regular polyacetals composed of *cis*-2,6-linked tetrahydropyran rings. Polymerization of 3(e)-benzyloxy-4(a)-methoxy-6,8-dioxabicyclo[3.2.1]octane (**1**) was undertaken in dichloromethane and toluene with phosphorus pentafluoride as initiator at −60°C. ^{13}C NMR analysis disclosed that the polymer predominantly consisted of the *cis*-2,6-linked tetrahydropyran rings **4β**. The proportions of the *cis* units in the polymers increased with decreasing initial monomer concentration. Polymerization of 3(e)-benzyloxy-6,8-dioxabicyclo[3.2.1]octane (**2**) was carried out in dichloromethane with phosphorus pentafluoride as initiator at −60 and −90°C. The polymers prepared at −60°C were enriched in the *cis* units **5β** as well, whereas the polymer entirely composed of the *trans*-2,6-linked tetrahydropyran rings **5α** was obtained at −90°C. These results were reasonably interpreted in terms of a previously proposed propagation mechanism involving oxonium exchange at the penultimate unit.

KEY WORDS Cationic Polymerization / Ring-Opening Polymerization / 6,8-Dioxabicyclo[3.2.1]octane / Bicyclic Acetal / Substituent Effect / Oxonium Exchange /

A number of structurally well-defined polysaccharides and their derivatives have been chemically synthesized by the cationic ring-opening polymerization of bicyclic acetals as well as anhydrosugar derivatives having a 6,8-dioxabicyclo[3.2.1]octane skeleton.[1-3] The polymerization of these compounds has provided valuable information on the stereochemistry and the reaction mechanism of the ring-opening polymerization of bicyclic acetals.[4,5] In most cases, the polymers obtained were predominantly or exclusively composed of *trans*-2,6-linked tetrahydropyran rings with an axially oriented exocyclic acetal oxygen (hereafter referred to as *trans* unit, α-form in the terminology of carbohydrate chemistry).

Several years ago, 3(e),4(a)-bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (**3**) was found to afford, under proper reaction conditions, a polymer consisting entirely of the *cis*-tetrahydropyran-2,6-diyloxymethylene units in which the exocyclic acetal oxygen was equatorially oriented (**6β**) (*cis* unit, β-form).[6,7] The polymer was converted by debenzylation to a polysaccharide, 4-deoxy-(1→6)-β-DL-*ribo*-hexopyranan.[6,7] This is indeed the first example for the synthesis of a (1→6)-β-linked polysaccharide by the ring-opening polymerization method. Recently, we proposed a propagation mechanism involving oxonium exchange for the specific formation of the *cis* unit in the polymerization of **3**.[8] In order to

substantiate the validity of the mchanism, polymerizations of 3(e)-benzyloxy-4(a)-methoxy-6.8-dioxabicyclo[3.2.1]octane (**1**) and 3(e)-benzyloxy-6,8-dioxabicyclo[3.2.1]octane (**2**) were investigated with particular emphasis on the steric control in the polymerization. This paper describes substituent effects on the stereochemical course related to the formation of polyacetals exclusively consisting of the *cis* units, especially the roles of the equatorial benzyloxy group in position 3 and the axial methoxy or benzyloxy groups in position 4.



EXPERIMENTAL

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

Dry benzene (50 ml) and 3(e),4(a)-dihydroxy-6,8-dioxabicyclo[3.2.1]octane (**7**) (8.6 g, 59 mmol) were placed in a three-necked flask equipped with a Dean–Stark trap and a condenser. *n*-Dibutyltin oxide (14.9 g, 59 mmol) was added to the solution, and the mixture was refluxed for 8 h. After the mixture was cooled to room temperature, benzyl bromide (11 g, 64 mmol) and tetrabutylammonium iodide (2.2 g, 6 mmol) were added to the solution. The mixture was heated at reflux temperature for 4 h. Other portions of benzyl bromide (6 g, 35 mmol) and tetrabutylammonium iodide (5.1 g, 14 mmol) were added, and the mixture was refluxed for further 3.5 h. Evaporation of the solvent afforded a viscous oil. It was purified by silica gel column chromatography (eluent, ethyl acetate–*n*-hexane = 1 : 1, v/v) and then recrystallized from ethanol. Yield, 8.5 g (61%); mp, 78—79°C. IR (KBr) cm^{-1}, 3300 ν_{O-H}, 3050 ν_{C-H} (arom.), and 1050 ν_{C-O} (ether); ^1H NMR ($CDCl_3$), δ 7.34 (s, 5H, C_6H_5), 5.50 (d, J = 2.2 Hz, 1H, H-5), 4.65—4.49 (m, 3H, H-1 and $C\underline{H}_2C_6H_5$), 3.89—3.74 (m, 2H, H-3 and H-4), 3.70 (s, 2H, 2H-7), 2.42 (d, J = 4.4 Hz, 1H, OH), 2.00—1.88 ppm (m, 2H, 2H-2); ^{13}C NMR ($CDCl_3$), δ 137.49 (C_6H_5, *ipso*), 128.30 (C_6H_5, *meta*), 127.27 (C_6H_5, *ortho* and *para*), 101.25 (C-5), 71.69 (C-1), 70.15 ($C\underline{H}_2C_6H_5$), 69.98 (C-4), 66.87 (C-3), 66.79 (C-7), and 31.93 ppm (C-2). *Anal.* Calcd for $C_{13}H_{16}O_4$: C, 66.09%; H, 6.83%. Found: C, 66.11%; H, 6.91%.

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

To a solution of **8** (4.7 g, 20 mmol) in 1,2-dimethoxyethane (30 ml) was added sodium hydride (60% in oil dispersion, 2.5 g, 63 mmol) which was washed twice with *n*-hexane. The mixture was stirred for 0.5 h at room temperature. Methyl iodide (4.5 g, 32 mmol) was added dropwise to the solution, and the mixture was stirred for 3.5 h at 35—40°C. After the reaction was quenched by the addition of methanol, the solvents were evaporated under reduced pressure. The residue was diluted with water (100 ml) and then extracted with four 50 ml portions of dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate. The mixture was filtered and the filtrate was freed from the solvent on a rotary evaporator. A crude oily product was purified by column chromatography on silica gel (eluent, ethyl acetate–*n*-hexane = 1 : 1, v/v). Yield, 3.8 g (76%). IR (liquid film) cm^{-1}, 3050 ν_{C-H} (arom.), 1100 ν_{C-O} (ether), 740 and 700 δ_{C-H} (monosubstituted phenyl); ^1H NMR ($CDCl_3$), δ 7.36—7.30 (m, 5H, C_6H_5), 5.53 (d, J = 2.7 Hz, 1H, H-5), 4.58 (d, J = 2.2 Hz, 2H, $C\underline{H}_2C_6H_5$), 4.55 (m, 1H, H-1), 3.85—3.71 (m, 1H, H-3), 3.67 (dd, J = 1.2 Hz, J = 4.2 Hz, 2H, 2H-7), 3.56 (s, 3H, CH_3), 3.49 (t, J = 3.1 Hz, 1H, H-4), 2.08 (t, J = 12.9 Hz, 1H, H-2), and 1.89–1.79 ppm (m, 1H, H-2); ^{13}C NMR

($CDCl_3$), δ 138.05 (C_6H_5, *ipso*), 128.16 (C_6H_5, *meta*), 127.43 and 127.27 (C_6H_5, *ortho* and *para*), 99.89 (C-5), 76.54 (C-1), 71.96 (C-4), 70.89 (C-3), 70.33 ($\underline{C}H_2C_6H_5$), 66.85 (C-7), 59.24 (CH_3), and 32.44 ppm (C-2).

Preparation of 3(e)-Benzyloxy-4(a)-(methylthio)thiocarbonyloxy-6,8-dioxabicyclo-[3.2.1]octane (**9**)

Imidazole (140 mg, 2 mmol) and **8** (6.0 g, 25 mmol) were dissolved in dry tetrahydrofuran (60 ml). Sodium hydride (60% in oil dispersion, 3.0 g, 75 mmol) was washed with *n*-hexane and added to the solution. The mixture was stirred for 2 h at room temperature. Carbon disulfide (12 ml) was added dropwise to the solution, and the reaction mixture was stirred for 1.5 h. After methyl iodide (12 g, 85 mmol) was cautiously dropped to the solution, the mixture was stirred for further 1.5 h. The reaction was stopped by the addition of water (100 ml). The resulting solution was extracted with two 50 ml portions of chloroform. The combined chloroform extracts were washed with successive 2% hydrochloric acid (100 ml) and saturated aqueous sodium hydrogencarbonate (100 ml). The organic layer was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by a rotary evaporator. The brown oily residue was crystallized from ethanol. Yield, 6.5 g (78%); mp, 91—94°C. IR (KBr) cm^{-1}, 1210 $\nu_{C=S}$, 740 and 700 δ_{C-H} (monosubstituted phenyl); ^1H NMR ($CDCl_3$), δ 7.34—7.24 (m, 5H, C_6H_5), 6.00 (t, $J=3.4$ Hz, 1H, H-4), 5.64 (d, $J=2.4$ Hz, 1H, H-5), 4.64 (s, 1H, H-1), 4.59 (d, $J=11.8$ Hz, 1H, $C\underline{H}_2C_6H_5$), 4.40 (d, $J=11.8$ Hz, 1H, $C\underline{H}_2C_6H_5$), 4.0—3.9 (m, 1H, H-3), 3.8—3.7 (m, 2H, 2H-7), 2.58 (s, 3H, CH_3), 2.13 (t, $J=12.4$ Hz, 1H, H-2), and 1.99—1.90 ppm (dd, $J=12.4$ Hz, $J=6.2$ Hz, 1H, H-2); ^{13}C NMR ($CDCl_3$), δ 215.39 (>C=S), 137.37 (C_6H_5, *ipso*), 128.16 (C_6H_5, *meta*), 127.47 (C_6H_5, *ortho* and *para*), 98.27 (C-5), 74.92 (C-1), 72.04 (C-4), 70.58 ($\underline{C}H_2C_6H_5$), 68.89 (C-3), 67.05 (C-7), 33.15 (C-2), and 18.83 ppm (CH_3).

Preparation of 3(e)-Benzyloxy-6,8-dioxabicyclo-[3.2.1]octane (**2**)

To a solution of **9** (6.3 g, 19 mmol) and azobis(isobutyronitrile) (50 mg) in toluene (500 ml) was added dropwise tri-*n*-butylstannane (11.5 g, 40 mmol) under a stream of nitrogen. The mixture was refluxed for 3 h, and additional tri-*n*-butylstannane (5 g, 17 mmol) was dropped. The mixture was refluxed for further 5 h. The solution was concentrated by a rotary evaporator. The residue was diluted with acetonitrile (200 ml). The solution was washed with five 50 ml portions of *n*-hexane. Removal of the solvent by a rotary evaporator gave **1** as a white crystal. It was chromatographed on silica gel (eluent, ethyl acetate–*n*-hexane = 1 : 2, v/v). The product was recrystallized from ethanol three times and finally from a mixed solvent of dichloromethane and *n*-hexane (1 : 2, v/v). Yield, 3.1 g (74%); mp, 60—61°C. IR (KBr) cm^{-1}, 1500 $\nu_{C=C}$ (phenyl), 740 and 700 δ_{C-H} (monosubstituted phenyl); ^1H NMR ($CDCl_3$) δ 7.31 (m, 5H, C_6H_5), 5.57 (s, 1H, H-5), 4.58 (m, 1H, H-1), 4.50 (s, 2H, $C\underline{H}_2C_6H_5$), 3.93 (m, 1H, H-3), 3.8—3.5 (m, 2H, 2H-7), 2.3—2.0 (m, 2H, H-2 and H-4), and 1.9—1.6 ppm (m, 2H, H-2 and H-4); ^{13}C NMR ($CDCl_3$), δ 138.15 (C_6H_5, *ispo*), 128.13 (C_6H_5, *meta*), 127.29 (C_6H_5, *ortho* and *para*), 100.84 (C-5), 72.81 (C-1), 69.94 ($\underline{C}H_2C_6H_5$), 69.18 (C-3), 68.02 (C-7), 38.57 (C-4), and 35.99 ppm (C-2). *Anal.* Calcd for $C_{13}H_{16}O_3$: C, 70.89%; H, 7.33%. Found: C, 70.91%; H, 7.46%.

Polymerization Procedures

Polymerizations were carried out using high vacuum technique. A solution of monomer in dichloromethane was dried over calcium hydride. The solution was transferred into a glass ampule and then it was concentrated to a prescribed initial monomer concentration. Phosphorus pentafluoride was generated by thermal decomposition of *p*-chlorobenzene-

diazonium hexafluorophosphate. The polymerization was terminated by the addition of a large volume of methanol. The polymer was purified by repeated reprecipitation using dichloromethane and methanol as a solvent–precipitant pair, and subsequent freeze-drying from a benzene solution.

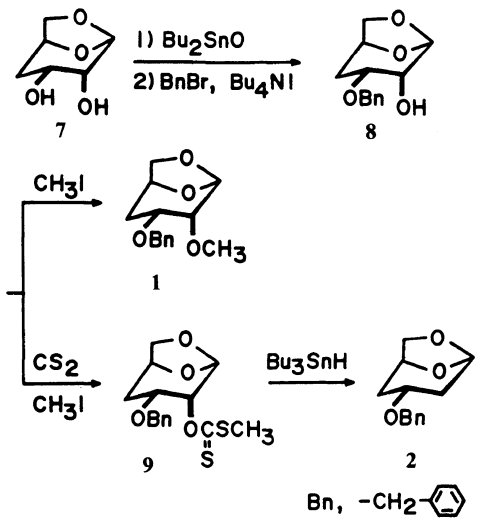
Characterization

^1H and ^{13}C NMR spectra were recorded on a JEOL FX-200 spectrometer working at 200 (^1H) and 50 MHz (^{13}C), respectively. Deuteriochloroform and tetramethylsilane were used as the solvent and internal reference, respectively. Molecular weights of the polymers were estimated by gel permeation chromatography (Column, Shodex A803 0.5 m plus A804 0.5 m; eluent, chloroform; polystyrene standard).

RESULTS AND DISCUSSION

Monomer Syntheses

3(e)-Benzyloxy-4(a)-methoxy-6,8-dioxabicyclo[3.2.1]octane (**1**) and 3(e)-benzyloxy-6,8-dioxabicyclo[3.2.1]octane (**2**) were synthesized from 3(e),4(a)-dihydroxy-6,8-dioxabicyclo[3.2.1]octane (**7**) as illustrated in Scheme I. The precursor **7** was prepared from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer) by the procedure described by Brown *et al.*[9] with some modifications. David *et al.*[10] reported selective benzylation of an equatorial hydroxyl group in monosaccharides. In a similar manner, benzylation of **7** gave 3(e)-benzyloxy-4(a)-hydroxy-6,8-dioxabicyclo-[3.2.1]octane (**8**). Subsequent methylation of **8** with sodium hydride and methyl iodide afforded bicyclic acetal **1** in 76% yield. Compound **2** was synthesized by radical deoxygenation of **8** according to the procedure improved by Barton *et al.*[11]: Thiocarbonyl ester **9** obtained from **8** was reduced with tri-*n*-butylstannane in the presence of azobis(isobutyronitrile) to produce monomer **2**.



Scheme I. Synthetic routes for 3(e)-benzyloxy-4(a)-methoxy-6,8-dioxabicyclo[3.2.1]octane (**1**) and 3(e)-benzyloxy-6,8-dioxabicyclo[3.2.1]octane (**2**).

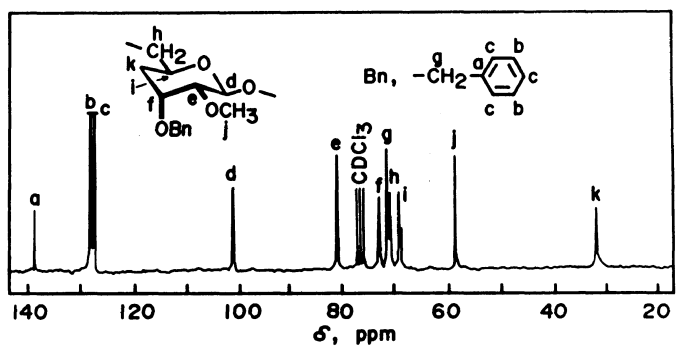


Figure 1. ^{13}C NMR spectrum of poly(4(a)-benzyloxy-3(e)-methoxytetrahydropyran-6,2-diyloxymethylene): Solvent, $CDCl_3$; temperature, 50°C; 50 MHz; internal reference, tetramethylsilane.

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

Solvent[b]	[Monomer]$_0$	Time	Yield	$\bar{M}_n$[c] $\times 10^{-4}$	*cis* Unit[d]
	mol l^{-1}	min	%		%
DM	2.0	15	92	6.0	72
DM	1.0	15	86	5.0	87
DM	0.5	120	70[e]	2.6	97
TL	0.5	120	12	6.6	93

[a] Monomer, 2 mmol (0.50 g); initiator, PF_5, 5 mol% to monomer; temp, −60°C.
[b] DM, dichloromethane; TL, toluene.
[c] Determined by gel permeation chromatography (polystyrene standard).
[d] Determined by ^{13}C NMR spectroscopy (anomeric carbon).
[e] *Anal.* Calcd for $(C_{14}H_{18}O_4)_n$: C, 67.18%; H, 7.28%. Found C, 67.03%; H, 7.35%.

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

Polymerization of **1** was undertaken in dichloromethane and toluene using phosphorus pentafluoride as the initiator at −60°C. Table I summarizes the results of the polymerization. The polymerization in dichloromethane proceeded rapidly and gave a white powdery polymer in a high yield. It was soluble in various solvents including benzene, chloroform, dimethylformamide, tetrahydrofuran, and 1,4-dioxane and insoluble in acetone and *n*-hexane.

Figure 1 shows the ^{13}C NMR spectrum of the polymer **4** prepared with the initial monomer concentration of 0.5 mol l^{-1}, together with the assignments of the signals. The ^{13}C NMR chemical shift data are compatible with the structure given in the figure (δ ($CDCl_3$): a, 138.37; b, 128.01; c, 127.29; d, 101.07; e, 81.24; f, 73.36; g, 71.74; h, 71.30; i, 69.49 and 69.06; j, 58.85; k, 32.36 ppm). From a comparison of these spectral data with those of the polymer **6β** obtained by the polymerization of 3(e),4(a)-bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane(**3**),[6-8] the appearance of the single acetal carbon signal at 101.07 ppm indicates that the polymer is almost exclusively composed of the *cis*-tetrahydropyran-2,6-diyloxymethylene units **4β** in which the exocyclic acetal oxygen is equatorially oriented. (IUPAC nomenclature, poly[4(a)-benzyloxy-3(e)-methoxytetrahydropyran-6,2-diyloxymethylene]). The one-bond coupling constant between the anomeric carbon and hydrogen $J_{C-1,H-1}$ gave additional evidence for the *cis*-linkage in the structural unit. In general, $J_{C-1,H-1}$ values of α- and β-glycosides are 170 and 160 Hz, respectively.[12,13] This empirical rule is applicable not only to monosaccharides but also to oligo- and polysaccharides. The polymer whose ^{13}C NMR spectrum is presented in Figure 1 gave a $J_{C-1,H-1}$ value of 161.1 Hz. Thus, it was demonstrated that the polymer was composed of the *cis*-2,6-linked tetrahydropyran ring (β-glycoside). The signal i splits into two peaks with different intensities. As monomer **1** is racemic, this splitting presumably originates from the different diad placements of the D,L-enantiomeric monomeric units in the polymer chain, as previously observed for the polymers of several bicyclic acetals.[7,14-17]

Two acetal carbon signals (97.15 and 101.07 ppm) appeared in the spectra of other polymers obtained under different conditions. This means the coexistence of the *cis* and *trans* units in these polymers. It should be noted that the proportion of the *cis* units in these polymers was appreciably changed, depending on the initial monomer concentration: The polymerization of **1** with lower initial monomer concentration afforded the polymer having a higher *cis* unit content. The dependence of the polymer structure on the initial monomer concentration will be discussed in a later section.

Polymerization of **1** in toluene proceeded more slowly than that in dichloromethane. The polymer obtained was also enriched in the *cis* units, but the *cis* unit content of the polymer was slightly lowered compared with that of the polymer prepared in dichloromethane

under otherwise identical conditions.

Polymerization of 3(e)-Benzyloxy-6,8-dioxabicyclo[3.2.1]octane (**2**)

Polymerization of **2** was carried out in dichloromethane at −60 and −90°C with phosphorus pentafluoride as the initiator. The results of the polymerization are listed in Table II. The polymerization proceeded smoothly at both temperatures and gave methanol-insoluble polymers (IUPAC nomenclature, poly[4(a)-benzyloxytetrahydropyran-2,6-diyloxymethylene]). The solubility of the polymers was similar to that of the polymer of **1**.

The ^{13}C NMR spectra of the polymers obtained under different conditions are presented in Figure 2. The ditailed ^{13}C NMR chemical shift data are listed in Table III. Two signals were observed in the acetal carbon region of the polymer prepared at −60°C (spectrum A). In the ^{13}C NMR spectra of polymers derived from bicyclic acetals including **1** and **3**, the acetal carbon signals of the *cis* units generally appear at several ppm downfield in comparison with the corresponding signals of the *trans* units.[16-20] Thus, the major

Table II. Polymerization of 3(e)-benzyloxy-6,8-dioxabicyclo[3.2.1]octane (**2**)[a]

$[Monomer]_0$	Temp	Time	Yield	$\bar{M}_n$[b] $\times 10^{-3}$	*cis* Unit[c]
mol l^{-1}	°C	min	%		%
1.0	−60	60	70	9.3	60
0.25	−60	40	20	7.1	81
0.20	−60	15[d]	6	5.1	89
2.0	−90	25	28[e]	35	0

[a] Monomer, 2 mmol (0.44 g); solvent, dichloromethane; initiator, PF_5, 5 mol% to monomer.
[b] Determined by gel permeation chromatography (polystyrene standard).
[c] Determined by ^{13}C NMR spectroscopy (anomeric carbon).
[d] Hours.
[e] *Anal.* Calcd for $(C_{13}H_{16}O_3)_n$: C, 70.89%; H, 7.33%. Found C, 70.81%; H, 7.31%.

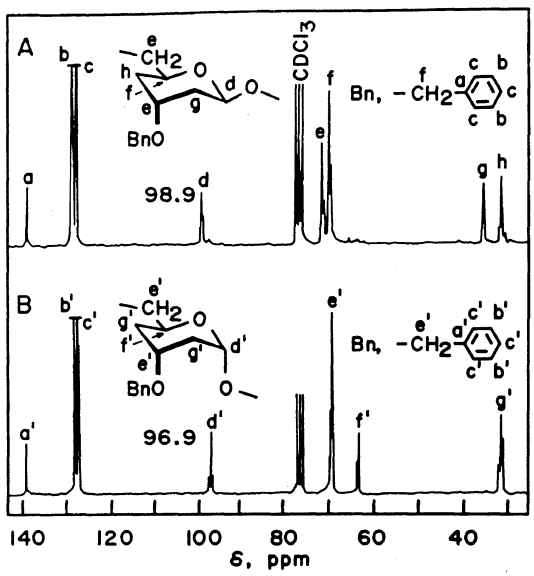


Figure 2. ^{13}C NMR spectra of poly(4(a)-benzyloxytetrahydropyran-2,6-diyloxymethylene): Solvent, $CDCl_3$; temperature, 50°C; 50 MHz; internal reference, tetramethylsilane. Polymerization conditions: A, solvent, dichloromethane; monomer concentration, 0.2 mol l^{-1}; initiator, phosphorus pentafluoride; temperature, −60°C. B, solvent, dichloromethane; monomer concentration, 2.0 mol l^{-1}; initiator, phosphorus pentafluoride; temperature, −90°C.

Table III. ^{13}C NMR chemical shift data of poly(4(a)-benzyloxytetrahydropyran-2,6-diyloxymethylene)

Structural unit	Assignment							
	a	b	c	d	e	f	g	h
5α	139.02	127.95	127.13	97.46 96.89 96.53	70.24 69.89 68.65	63.97 63.61	32.65 31.97 31.66	
5β	138.57	128.12	127.17	98.85	71.88 71.18	70.07 69.76	35.74	31.83

signal d can be assigned to the *cis*-2,6-linked tetrahydropyran ring **5β** in which the exocyclic oxygen is equatorially located. The minor peak (not marked) at a higher field of the signal d is assignable to the acetal carbon of the *trans* unit. As easily noticeable from this spectrum, the polymerization of **2** at −60°C also gave the polymer enriched in the *cis* units as in the polymerization of **1** and **3**.[6-8] Further, the proportion of the *cis* units in the polymer of **2** also increased with decrease in the initial monomer concentration (Table II). However, **2** afforded the polymer having a *cis* unit content of at most 89% even when the initial monomer concentration was as low as 0.2 mol l^{-1}, while the polymerization of **1** with the initial monomer concentration of 0.5 mol l^{-1} gave the polymer almost entirely composed of the *cis* units.

The polymer prepared at −90°C (spectrum B) shows essentially one signal d′ in this region, indicating that the polymer entirely consists of the *trans* unit **5α** in which the exocyclic acetal oxygen is axially oriented. Strictly speaking, the signal d′ splits into three peaks. Although definite assignments cannot be made at present, this splitting seems to arise from the different triad placements of the D,L-enantiomeric monomeric units in the polymer chain by the analogy of the polymers of bicyclic acetals including **1** and **3**.[7,14-17]

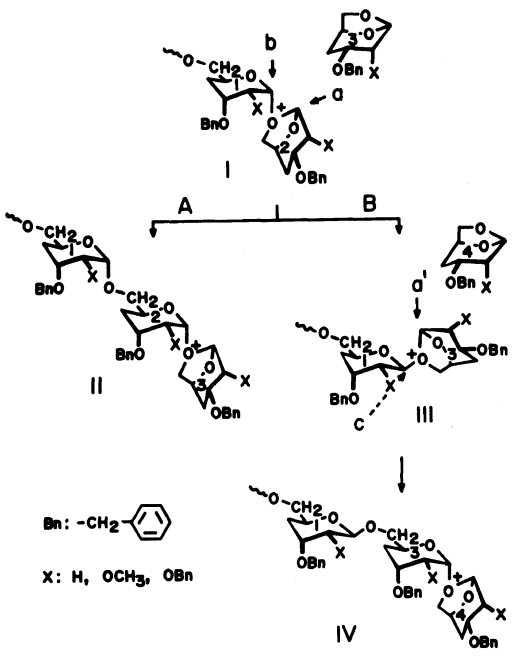
The chemical shifts of the other carbons as well as the acetal carbon were affected by the difference in the glycosidic linkages in the polymer chains. Each carbon in the *trans* unit showed a peak at a higher field of the corresponding peak of the *cis* unit. Especially, the peak f′ showed a 6.5 ppm upfield shift from the peak f of the *cis* unit due to the steric compression effect.

Substituent Effect of an Equatorially Oriented Benzyloxy Group in Position 3

Very recently, we reported the polymerization behavior of **3** having likewise an equatorial benzyloxy group in position 3.[8] The polymerization of monomers **1** and **2** is similar to that of **3** in the following three points: (i) These monomers gave the polymers enriched in the *cis*-2,6-linked tetrahydropyran rings at −60°C. (ii) The proportion of the *cis* units in the polymers increased with decreasing initial monomer concentration. (iii) The polymerization with higher monomer concentration and at lower temperature yielded the polymers predominantly composed of the *trans* units: As in the polymerization of **2** at −90°C, the polymerization of **3** at −90°C was found to produce the polymer exclusively composed of the trans units **6α** (initial monomer concentration; 1.8 mol l^{-1}; solvent, dichloromethane; initiator, antimony pentachloride).[8] From the aforementioned resemblances in the polymerizations of these three monomers, it seems reasonable to assume that they proceed through a similar propagation process. All these three monomers possess, as a common substituent, an equatorially oriented benzyloxy group in position 3 and therefore this substituent undoubtedly plays an important role in the formation of the structurally regular polymers containing the *cis*-tetrahydropyran-2,6-diyloxymethylene units. In fact, unsubstituted 6,8-dioxabicyclo[3.2.1]octane gave a polymer entirely composed of the *trans* units at −60°C under identical conditions with those for the polymerization of **2** (initial monomer concentration, 0.25 mol l^{-1}; initiator, phosphorus pentafluoride).

The specific formation of the *cis*-2,6-linked units observed in the polymerization of monomers **1**, **2**, and **3** can be reasonably interpreted by taking into consideration thermodynamical equilibrium between monomer and polymer. As in the polymerization of other bicyclic acetals with the same skeleton at low tempertures, an ordinary S_N2 type cleavage at the C(5)–O(6) bond in the polymerization of **1**—**3** should yield the polymers composed of the trans-2,6-linked tetrahydropyran rings (**4α**—**6α**).

However, there is an energetically very un-



Scheme II. Propagation processes in the polymerization of 3(e)-benzyloxylated 6,8-dioxabicyclo[3.2.1]octane derivatives (**1**, **2**, and **3**).

favorable 1,3-diaxial nonbonded repulsion between the ether oxygen of the axially oriented benzyloxy group and the exocyclic acetal oxygen atom in each *trans* unit. Therefore, the free energy difference between the *trans* unit and its monomer must be relatively small. As a consequence, the reverse reaction, that is, the ring-closure of the *trans* unit to the momomer (depolymerization), would occur relatively easily in the polymerization of these monomers. A possible propagation mechanism common to the polymerization of these monomers is illustrated in Scheme II by the analogy with the recently proposed mechanism for the polymerization of **3**.[8]

In cationic polymerization of bicyclic acetals, a growing chain end is reasonably postulated to be a cyclic trialkyloxonium ion **I**. The monomeric unit 1 is incorporated into the polymer chain as a trans unit when monomer 3 attacks the acetal carbon of the growing chain end unit 2 in the oxonium ion I from the opposite direction of the $C–O^+$ bond to give II (arrow a, path A). In the structure **I**, however, there is a severe 1,3-diaxial nonbonded interaction between the oxonium oxygen atom in the terminal unit 2 and the ether oxygen of the axial benzyloxy group in the penultimate unit 1. Therefore, the acetal carbon in the *trans*-type penultimate unit 1 is susceptible to nucleophilic reactions from the direction of the arrow b to relieve the repulsion. If the exocyclic oxygen of the same unit attacks this carbon, an internal ring-closure reaction (depolymerization) occurs. Alternatively, when monomer 3 attacks from the same direction b, the monomeric unit 1 is transformed to a *cis*-type penultimate unit through path B (oxonium exchange). In the oxonium ion **III**, monomer addition from the direction of the broken arrow c must be highly retarded bacause of the steric hindrance due to the bulky substituents in the penultimate unit 1. Consequently, subsequent monomer addition is forced to take place predominantly from the direction of arrow a′ onto the acetal carbon of the terminal unit 3. By this monomer addition, the monomeric unit 1 is incorporated into the polymer chain as a *cis* unit and the oxonium ion **I** with the degree of polymerization increased by one (structure **IV**) is reproduced. Thus, the regular repetition of the reaction sequence (**I**→**III**→**IV**) through path B gives the polymer composed of the *cis*-2,6-linked tetrahydropyran rings in the main chain.

The dependence of the proportion of the *cis* units in the polymers on initial monomer concentration is also reasonably explained on the basis of this reaction mechanism. The equilibrium between the propagation to form the *trans* unit and the internal ring-closure reaction is thermodynamically related to the initial monomer concentration. In the polymerization with sufficiently high initial monomer concentration, the *trans* units are predominantly formed by the preferential propagation *via* path A. With decreasing initial monomer concentration, the formation of the

trans units becomes retarded or prohibited by the increasing contribution of the depolymerization. On the other hand, the formation of the *cis* unit can take place even at lower initial monomer concentration, competing with the internal ring-closure. The reason is that 1,3-diaxial oxygen–oxygen nonbonded interaction is absent in any *cis* unit derived from monomers **1**—**3**, so that the free energy difference between each monomer and its *cis* unit is larger than that for the corresponding *trans* unit. Therefore, the lower the initial monomer concentration, the higher becomes the fraction of the *cis* units in the polymer by the preferential propagation *via* path B.

The axial substituent in position 4 in monomers **1** and **3**, the methoxy and benzyloxy groups, respectively, should affect more or less the equilibrium between monomer and polymer. Probably the monomer–polymer equilibrium in the polymerizations of monomers **1** and **3** is displaced further to the monomer side than that in the polymerization of **2**. Moreover, monomer addition from the direction of arrow a in Scheme II in the polymerization of **1** and **3** should be more strongly retarded by the steric hindrance due to these axial substituents than that in the polymerization of **2**. As a result, the propagation *via* path B took place more easily in the polymerization of **1** and **3** and these two monomers gave polymers containing higher fractions of the corresponding *cis* units than **2** did.

The polymerization of **2** and **3** at $-90°C$ should be briefly discussed. Although the exact conformation at the transition state for the oxonium exchange (**I**→**III**) is not known, the tetrahydropyran ring of the penultimate unit 1 probably takes a somewhat skewed conformation so as to minimize the nonbonded interaction between the axial benzyloxy group and the departing monomer unit 2. Because of the intervention of this process requiring higher activation energy, the propagation *via* path B to form the *cis* unit is retarded at lower temperture, and the kinetically more favorable propagation *via* path A takes place preferentially to produce the *trans* unit. With increasing initial monomer concentration, the propagation *via* path A should be accelerated. Thus, the polymerization of **2** and **3** at $-90°C$ at a higher initial monomer concentration gave the polymers entirely composed of the *trans*-2,6-linked tetrahydropyran rings **5α** and **6α**, respectively.

In summary, the cationic ring-opening polymerization of **1** and **2** at $-60°C$ gave the corresponding polyacetals predominantly containing the *cis*-2,6-linked tetrahydropyran rings. As in the polymerization of **3**, the formation of the *cis* units in the polymerization of **1** and **2** is reasonably explained by an S_N2 type propagation process accompanied by the oxonium exchange at the penultimate unit. All these three monomers possess, as a common substituent, an equatorially oriented benzyloxy group in position 3, and therefore this substituent undoubtedly plays an important role in the sterically controlled specific propagation described above.

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