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Polymerization of Bicyclic Acetals. 15. Propagation Process Accompanied by Oxonium Exchange in the Cationic Polymerization of 3(e),4(a)-Bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane

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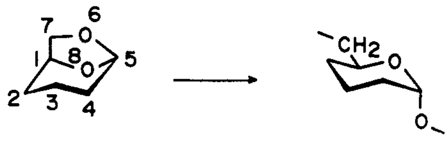
ABSTRACT: A propagation mechanism involving oxonium exchange was proposed for the specific formation of polyacetal exclusively consisting of the *cis*-tetrahydropyran-2,6-diyloxymethylene backbone structure (**4β**) in the cationic ring-opening polymerization of 3(e),4(a)-bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (**3**). The polymerization of **3** was carried out under various conditions (solvent, dichloromethane and toluene; initiator, phosphorus pentafluoride, antimony pentachloride, and trifluoromethanesulfonic acid; temperature range, -90 to -30 °C). The structures of the polymers were examined by ^{13}C NMR spectroscopy. The polymerization with lower initial monomer concentration at or above -60 °C gave the polymers entirely composed of the cis units, whereas lowering the temperature or increasing the initial monomer concentration favored the formation of the *trans*-tetrahydropyran-2,6-diyloxymethylene unit (**4α**). The polymerization in higher initial monomer concentration at -90 °C gave the polymer completely consisting of the trans units. The formation of the cis unit **4β** in the polymerization of **3** was interpreted in terms of S_N2 type propagation accompanied by oxonium exchange at the penultimate unit of the polymer chain.

Introduction

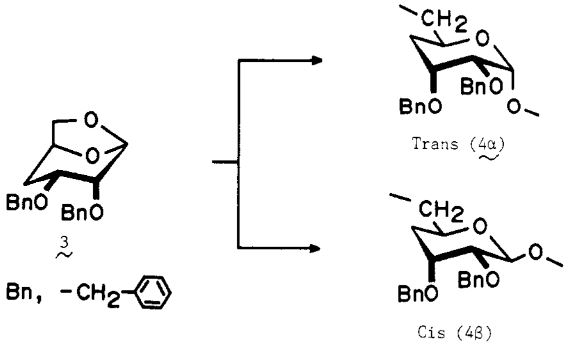
Cationic ring-opening polymerization of anhydrosugar derivatives having a bicyclic acetal skeleton has been established as one of the most useful methods for the chemical synthesis of polysaccharides with high molecular weights and well-defined structures.[1-3] In relation to the chemical synthesis of stereoregular polysaccharides, some important and interesting information has been obtained on the stereoregulation in the cationic polymerization of bicyclic acetals.[4-9] Thus, the polymerization of the parent compound of 1,6-anhydrosugars, 6,8-dioxabicyclo[3.2.1]octane (**1**), proceeds through an S_N2 type propagation mechanism involving the selective C(5)-O(6) bond cleavage of a growing cyclic trialkyloxonium ion at low temperature to produce a trans-2,6-linked polymer in which the exocyclic acetal oxygen was axially oriented to the tetrahydropyran ring in the repeating unit (**2**, (1→6)-α-pyranosyl residue in the terminology of carbohydrate chemistry).



1 2

A number of bicyclic acetals and anhydrosugar derivatives having the same skeleton showed similar behaviors in their polymerizations. Therefore, it has been difficult to synthesize structurally regular polymers containing a cis-2,6-linked tetrahydropyran ring in the repeating unit (β-pyranosyl residue) in which the exocyclic acetal oxygen was located equatorially to the tetrahydropyran ring. There have been some reports[4,10,11] referring to the formation of the cis structural units from **1** and related monomers. However, all these papers were based on the recognition that these cis units were produced by side reactions, because in most cases the cis units were formed only as a minor component in the polymerization at higher temperatures.

Among bicyclic acetals having a bicyclo[3.2.1]octane skeleton, 3(e),4(a)-bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (**3**, 1,6-anhydro-2,3-di-*O*-benzyl-4-deoxy-β-DL-*ribo*-hexopyranose in the nomenclature of carbohydrate chemistry) was recently found to give a polymer entirely composed of cis-2,6-linked tetrahydropyran rings **4β** in the polymerization using phosphorus pentafluoride as an in-



3
Trans (4α)
Cis (4β)

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itiator at −60 °C.[12] Subsequent debenzylation of the resulting polymer afforded 4-deoxy-(1→6)-β-DL-*ribo*-hexopyranan. This is the first example of a (1→6)-β-linked synthetic polysaccharide by the ring-opening polymerization method. The corresponding (1→6)-β-L-polysaccharide was also synthesized by the ring-opening polymerization of the L enantiomer of **3**.[13]

For clarification of the cause for the specific formation of the cis-linked polymers, the polymerization of **3** was carried out under a variety of reaction conditions, and the structures of the resulting polymers were examined by ^{13}C NMR spectroscopy. The present paper discusses the stereochemical course of the cationic ring-opening polymerization of **3**, especially the propagation mechanism for the formation of the polymer containing the cis-2,6-linked tetrahydropyran ring **4β** in the repeating unit.[14]

Experimental Section

Materials. Monomer **3** was synthesized from 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer) via five reaction steps. The precursor of **3**, 3(e),4(a)-dihydroxy-6,8-dioxabicyclo[3.2.1]octane was prepared by the method of Brown et al.[15-17] with some modifications.

Preparation of 3(e),4(a)-Bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (3). Sodium hydride (60% in oil dispersion, 3.8 g, 95 mmol) was washed with *n*-hexane and added to a solution of 3(e),4(a)-dihydroxy-6,8-dioxabicyclo[3.2.1]octane (4.6 g, 32 mmol) in dry *N*,*N*-dimethylformamide (50 mL). The mixture was stirred for 0.5 h at room temperature and then heated to 60 °C. Benzyl chloride (18.0 g, 142 mmol) was added dropwise to the solution, and the reaction mixture was heated at 60 °C for 1 h. After having been cooled to room temperature, the mixture was poured into ice water (500 mL) and then extracted with four 100-mL portions of chloroform. The combined chloroform extracts were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to afford a viscous oil. It was purified by silica gel column chromatography (eluent, ethyl acetate:*n*-hexane, 1:1 v/v). The product was recrystallized from ethanol three times and finally from a mixed solvent of dichloromethane and *n*-hexane (2:1 v/v); mp 43–44 °C.

Polymerization Procedure. Polymerization of **3** was undertaken at temperatures between −90 and −30 °C by using a high-vacuum technique. Phosphorus pentafluoride, antimony pentachloride, and trifluoromethanesulfonic acid were employed as the initiators. The polymerization was carried out in a sealed ampule for an appropriate period. The polymerization was terminated by the addition of a large volume of methanol. The polymer was purified by repeated reprecipitation with dichloromethane and methanol as a solvent–precipitant pair, followed by freeze-drying from a benzene solution. ^{13}C NMR (CH_2Cl_2, D_2O external lock): **4α**, δ 139.74 and 138.85 (C_6H_5, ipso), 128.40 (C_6H_5, meta), 127.58 (C_6H_5, ortho and para), 97.89 (C-2), 77.07 (C-3), 72.33 (C-4), 71.76 and 71.20 ($CH_2C_6H_5$), 70.05 (OCH_2), 64.31 (C-6), 31.56 (C-5); **4β**, δ 139.16 (C_6H_5, ipso), 128.28 (C_6H_5, meta), 127.62 (C_6H_5, ortho and para), 101.44 (C-2), 79.36 (C-3), 77.44 (C-4), 72.91 and 72.02 ($CH_2C_6H_5$), 71.47 (OCH_2), 69.82 (C-6), 32.28 (C-5).

Isomerization of Polymer. A solution of polymer in dichloromethane was dried over calcium hydride in a high-vacuum line. The solution was transferred into a glass ampule, and then phosphorus pentafluoride was added. The ampule was sealed and kept at −60 °C for 10 days. Pyridine and methanol were added to quench the reaction. The solution diluted with dichloromethane was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure. The residue was poured into a large volume of methanol to precipitate the polymer. The polymer was purified in a manner similar to the procedure described above.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-200 spectrometer operating at 200 (^1H) and 50 MHz (^{13}C). Deuteriochloroform and dichloromethane (D_2O as an external lock compound) were used as the solvents. Tetramethylsilane was employed for internal reference. Molecular weights of the polymers were measured by gel permeation chromatography with a Hitachi 634A high-performance liquid chromatograph (column, Shodex 80M, 1 m; polystyrene standard; eluent, chloroform).

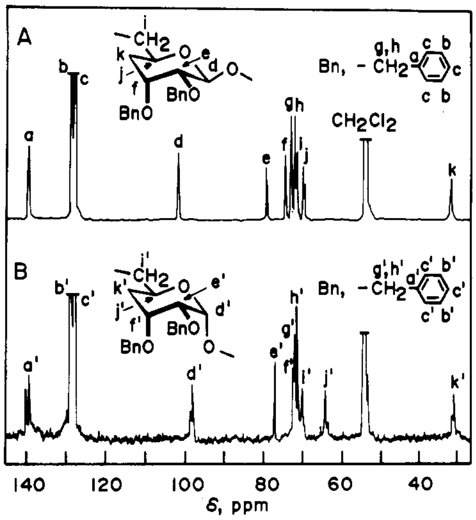


Figure 1. ^{13}C NMR spectra of poly(3(e),4(a)-bis(benzyloxy)-tetrahydropyran-6,2-diyloxymethylene): solvent, CH_2Cl_2; external lock, D_2O; room temperature; 50 MHz; internal reference, tetramethylsilane. Polymerization conditions: A, solvent, dichloromethane; monomer concentration, 0.57 mol/L; initiator, phosphorus pentafluoride; temperature, −60 °C. B, solvent, dichloromethane; monomer concentration, 1.8 mol/L; initiator, antimony pentachloride; temperature, −90 °C.

Results and Discussion

Polymerization of 3(e),4(a)-Bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (3). Polymerization of **3** was undertaken at different temperatures ranging from −90 to −30 °C. Figure 1 shows the ^{13}C NMR spectra of the polymers (IUPAC nomenclature, poly[3(e),4(a)-bis(benzyloxy)tetrahydropyran-6,2-diyloxymethylene]) obtained in dichloromethane under different conditions. Both spectra show essentially only one signal in the anomeric carbon region (d and d′), indicating that these polymers possess high structural regularities.[18]

The anomeric configuration of pyranoses can be determined from both the chemical shift of the anomeric carbon and the one-bond coupling constant between the anomeric carbon and hydrogen atoms, $J_{C\text{-}1,H\text{-}1}$.[19,20] The anomeric chemical shift (δ 101.44) of the polymer prepared at −60 °C in dilute solution with phosphorus pentafluoride as the initiator (spectrum A) corresponds to those for methyl β-D-glucopyranoside (δ 102.6[21]), methyl β-D-allopyranoside (δ 101.9[20]), and pustulan (δ 102.7[22]), which is a polysaccharide composed of (1→6)-β-linked glucose units. It is generally accepted as an empirical rule that α-glycosides with an equatorial anomeric hydrogen give a $J_{C\text{-}1,H\text{-}1}$ value of 170 Hz, whereas β-glycosides with an axial anomeric hydrogen give a $J_{C\text{-}1,H\text{-}1}$ value of 160 Hz.[19,20,23] For instance, (1→6)-β-linked pustulan shows a $J_{C\text{-}1,H\text{-}1}$ value of 160 Hz,[22] while both (1→6)-α-linked dextran and its tribenzylated derivative show a $J_{C\text{-}1,H\text{-}1}$ value of 171 Hz.[24] The polymer prepared at −60 °C in dilute solution with phosphorus pentafluoride as the initiator (spectrum A) gave a $J_{C\text{-}1,H\text{-}1}$ value of 162.1 Hz. Thus, it was substantiated that the polymer was composed of the cis-2,6-linked tetrahydropyran rings having the equatorially oriented exocyclic acetal oxygen (β-pyranosyl residue). On the other hand, the polymer obtained at −90 °C in more concentrated solution with antimony pentachloride as the initiator (spectrum B) showed the acetal carbon signal at δ 97.89, which was in good agreement with those of the structurally regular polymers having the "α-configuration" derived from

Table I
Polymerization of 3(e),4(a)-Bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (3) in Dichloromethane[a]

run no.	monomer, mol/L		initiator, mol%	temp, °C	time, min	yield, %	$10^{-4} \times M_n$[b]	M_w/M_n[b]	cis unit,[c] %
1	0.57	PF_5	5	-30	120	28	0.58	1.9	100
2	2.2	PF_5	5	-60	20	82	2.4	2.8	71
3	1.3	PF_5	5	-60	20	91	2.0	2.2	90
4	0.57	PF_5	5	-60	80	79	1.8	1.8	100
5	0.57	PF_5	5	-60	24[d]	88	1.1	1.7	100
6	0.57	$SbCl_5$	5	-60	20[d]	76	1.2	2.0	100
7	0.57	CF_3SO_3H	5	-60	20[d]	28	1.0	1.8	100
8	0.30	PF_5	5	-60	180	61	1.3	1.9	100
9	1.3	PF_5	5	-78	80	9	15.6	2.0	44
10	0.57	PF_5	5	-78	180	2.	7.6	2.0	81
11	0.57	PF_5	5	-78	24[d]	92	3.5	2.2	88
12	1.8	PF_5	5	-90	240	7	2.6	2.1	15
13	1.8	PF_5	5	-90	24[d]	74	3.4	2.6	49
14	1.8	$SbCl_5$	5	-90	120	5	2.0	2.0	0

[a] Monomer, 2 mmol (0.65 g) except for number 8 (monomer, 1 mmol (0.33 g)). [b] Determined by gel permeation chromatography (polystyrene standard). [c] Determined by ^{13}C NMR spectroscopy (anomeric carbon). [d] Hours.

Table II
Polymerization of 3(e),4(a)-Bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (3) in Toluene[a]

monomer, mol/L	temp, °C	time, min	yield, %	$10^{-4} \times M_n$[b]	M_w/M_n[b]	cis unit,[c] %
0.57	-30	10	55	2.6	2.6	100
0.57	-60	40	13	3.3	3.3	81
0.30	-60	40	11	2.9	2.4	86
0.30	-60	100	29	3.3	3.7	93
0.13	-60	20[d]	72	10.0	2.5	100

[a] Monomer, 2 mmol (0.65 g); initiator, phosphorus pentafluoride, 5 mol % to monomer. [b] Determined by gel permeation chromatography (polystyrene standard). [c] Determined by ^{13}C NMR spectroscopy (anomeric carbon). [d] Hours.

Table III
Isomerization of Poly(3(e),4(a)-bis(benzyloxy)tetrahydropyran-6,2-diyloxymethylene)[a]

original polymer			recovered polymer	
M_n[b]	cis unit,[c] %	$[monomer]_r$,[d] mol/L	M_n[b]	cis unit,[c] %
18000	100	0.035	7300	100
16000	28	0.030	5900	100

[a] Reaction conditions: polymer, 1 base mmol (0.33 g); 0.5 base mol/L solution in dichloromethane; temperature, -60 °C; catalyst, phosphorus pentafluoride, 0.2 mmol; time, 10 days. [b] Determined by gel permeation chromatography (polystyrene standard). [c] Determined by ^{13}C NMR spectroscopy. [d] Concentration of monomer formed by depolymerization; estimated by ^1H NMR spectroscopy.

a number of bicyclic acetals and 1,6-anhydrosugar derivatives with the same backbone structures. Therefore, it was confirmed that the polymer was entirely composed of the trans structural units with the axially oriented exocyclic acetal oxygen in the repeating unit 4α.

Table I summarizes some of the results of the polymerization in dichloromethane. It is noteworthy that the proportions of the cis and trans units in the polymers were significantly changed with initial monomer concentration and polymerization temperature. The polymers prepared at or above -60 °C were enriched in the cis units (numbers 1-8). Polymerization with lower initial monomer concentration gave the polymers containing a higher fraction of the cis unit. Especially, the polymerization with the initial monomer concentrations less than 0.57 mol/L gave the regularly cis-2,6-linked polymers. The polymers exclusively composed of the cis units were obtained independent of the initiators (numbers 5-7). The trans unit content in the polymer increased with lower temperatures (cf. numbers 5, 11, 13).

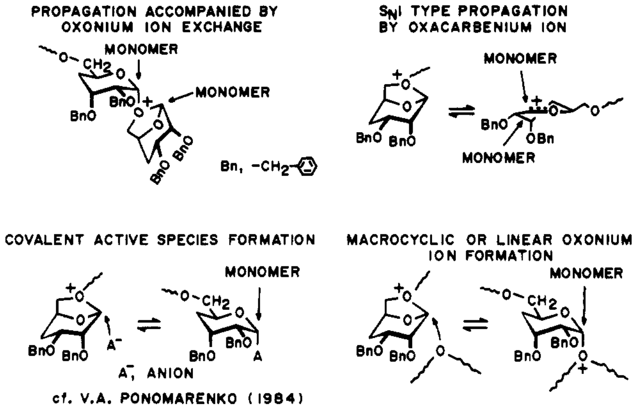
The polymerization at -90 °C with antimony pentachloride as the initiator gave the polymer perfectly consisting of the trans units (number 14). When phosphorus pentafluoride was employed as the initiator, polymers containing both the trans and cis units were produced even at -90 °C (number 12). The trans unit content in the polymer decreased in the polymerization for a longer reaction time (number 13).

The results of the polymerization of 3 in toluene are listed in Table II. The polymer entirely composed of the cis units was afforded by the polymerization at -30 °C in toluene as well as in dichloromethane. However, structurally irregular polymers were obtained at -60 °C in toluene even when the initial monomer concentration was 0.57 mol/L. For synthesis of the structurally controlled cis-2,6-linked polymer, a more dilute monomer solution (0.13 mol/L) was needed.

As briefly described above, prolonged polymerization caused appreciable decrease in the trans unit content of the polymer. Isomerization of the polymers was therefore investigated to clarify this phenomenon. The results are presented in Table III.

The reaction was carried out in dichloromethane at -60 °C in the presence of phosphorus pentafluoride. Two polymer samples with similar molecular weights but different contents of the cis unit were employed; that is, one was entirely composed of the cis units and the other was rich in the trans units. The initial polymer concentration (0.5 base mol/L) was adjusted so as to correspond to the initial monomer concentration in which the cis-2,6-linked polymer was selectively formed in the polymerization. The polymer exclusively consisting of the cis units maintained its structural regularity throughout the reaction but showed appreciable depression in the molecular weight. On the contrary, the polymer having the trans unit content of 72% was transformed to the entirely cis-2,6-linked polymer. These results indicate that the trans unit is thermodynamically less stable than the cis unit. The ring-opening reaction of the monomer 3 to form the trans unit 4α brings about energetical stabilization due to the anomeric effect on the one hand, but it produces unfavorable 1,3-diaxal nonbonding repulsion between the exocyclic acetal oxygen atom and the oxygen atom of the axial benzyloxy group on the other hand. Conceivably, the isomerization of the trans unit to the cis unit takes place to release this repulsion.

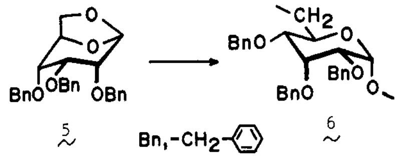
Scheme I
Possible Reactions for the Cis Unit Formation in the Polymerization of 3(e),4(a)-Bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (3)



Polymerization Mechanism. On the basis of the foregoing results, the propagation mechanism in the cationic ring-opening polymerization of 3 is discussed. In the polymerization of bicyclic acetals having a bicyclo[3.2.1]octane skeleton, it has been reasonably postulated that the structurally regular polymers composed of the trans units are formed by the S_N2 type propagation involving a trialkyloxonium ion.[2,3,10] On the other hand, four concepts shown in Scheme I have been proposed to explain the formation of the cis units in the polymers.

The first is the participation of oxacarbenium ions produced by the unimolecular cleavage of cyclic trialkyloxonium ions: The growing trialkyloxonium ion of 3 may undergo a unimolecular cleavage to form an oxacarbenium ion because of the steric and electronic repulsions between the two benzyloxy groups (Scheme I, upper right). However, even if this reaction occurred, it would be very unlikely that a structurally regular polymer is formed from this ion because the attack of monomer is feasible from either side of the nearly planar structure.

Uryu et al.[25] synthesized a stereoregular polysaccharide by the cationic polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-*β*-D-allopyranose (5) possessing an additional, axially oriented benzyloxy group compared with 3. The formation of the trans-2,6-linked polymer (6, 2,3,4-tri-*O*-benzyl-(1→6)-*α*-D-allopyranan by the terminology in carbohydrate chemistry) can be explained by the conventional S_N2 type propagation mechanism involving a cyclic trialkyloxonium ion. In view of the fact that steric and electronic repulsions between the bulky substituents in 5 must be larger than those in 3, the formation of 6 strongly suggests that the oxacarbenium ion mechanism is not operative in the polymerization of 3, having a structure similar to that of 5.



All the other three concepts involve cyclic trialkyloxonium ions as the growing chain ends. Ponomarenko et al.[10] proposed a propagation mechanism for the formation of the cis units (at most 35%) in the polymerization of 1,6-anhydroglucose derivatives with several initiators: In the case of the initiators whose counteranions are more nucleophilic than monomers, such as trityl perchlorate or triflic anhydride, a counteranion would react with a growing chain end to afford a covalent species with trans configuration. Subsequent S_N2 type attack of monomer to the anomeric carbon of the covalent species produces the cis units in the polymer. According to their mechanism, possible reaction for the formation of the cis unit in the polymerization of 3 is shown in the lower left part of Scheme I. However, the polymerization of 3 initiated with phosphorus pentafluoride yielding a less nucleophilic counteranion as well as with trifluoromethanesulfonic acid gave the predominantly cis-2,6-linked polymers. Therefore, this result cannot be accounted for by their mechanism.

Macrocyclic or linear trialkyloxonium ions formed by inter- or intramolecular reactions between a growing cyclic trialkyloxonium ion and an acetal oxygen atom in a polymer chain may give a cis structural unit by trans-acetalization (Scheme I, lower right).[4,10] However, such trans-acetalization should lead to polymers containing both the cis and trans units in various proportions.

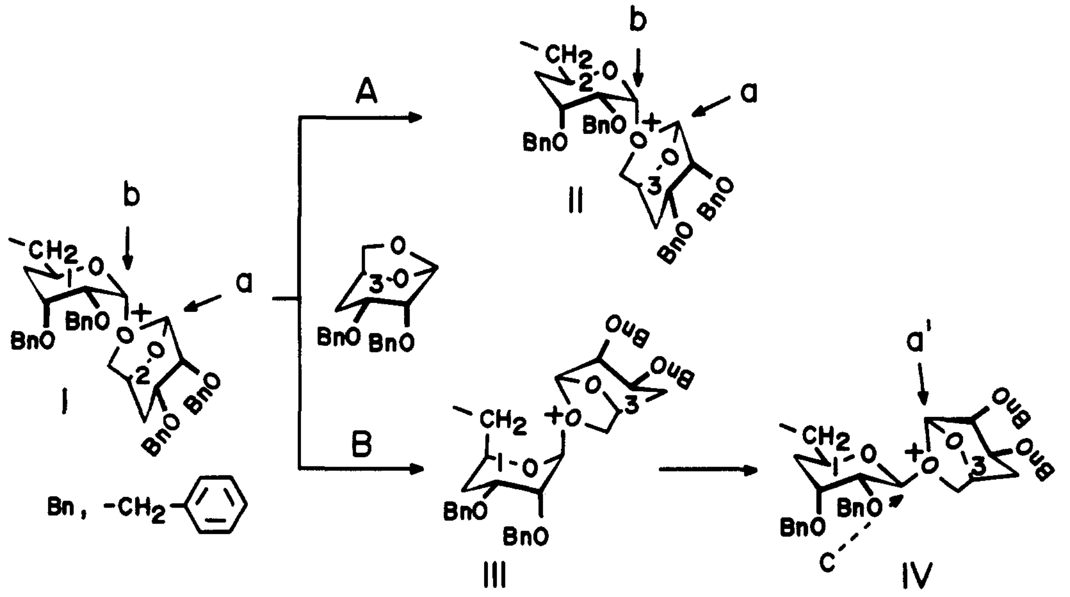
Oxonium-exchange reactions are common in the cationic ring-opening polymerization of cyclic ethers and acetals.[26] It is merely monomer exchange for monocyclic monomers, but it is accompanied by the transformation of the cis linkage to the trans linkage or vice versa in the repeating units for bicyclic compounds. A probable and rational reaction that can satisfactorily explain the polymerization behavior of 3 is S_N2 type propagation accompanied by oxonium exchange on the acetal carbon of the penultimate unit (Scheme I, upper left). The regular repetition of the reaction sequence (I → III → IV) shown in Scheme II would give rise to the polymer entirely consisting of the cis units.

The monomeric unit 2 in the chain end was incorporated into the polymer chain as a trans unit when monomer 3 attacks the acetal carbon of the cyclic oxonium ion **I** from the opposite direction of the C–O⁺ bond (arrow a, path A). On the contrary, when S_N2 type attack of monomer 3 takes place on the acetal carbon of the penultimate unit 1 (oxonium exchange), the monomeric unit 1 is transformed with ring inversion to a cis unit (arrow b, path B). The structure III, being of conformationally high energy, is rapidly converted to the energetically more stable structure IV. Subsequent monomer addition to the chain end unit 3 in the oxonium ion **IV** (arrow a′) reproduces the oxonium ion I, with the degree of polymerization increased by one. Monomer addition to the penultimate unit in the oxonium ion IV (broken arrow c) should result in oxonium exchange. However, this reaction is strongly retarded because of the steric hindrance by the two benzyloxy groups in the penultimate unit 1. Therefore, the attack of the monomer occurs preferentially on the acetal carbon of the growing chain end unit 3 of the oxonium ion IV from the direction of the arrow a′.

The polymer structures varied widely depending on the initial monomer concentrations and polymerization temperatures. The propagation mechanism proposed above gives a rational explanation to these phenomena. First, let us consider the effect of the initial monomer concentration on the polymerization behavior of 3. In Scheme II, two types of reactions can take place competitively on the penultimate unit 1 (arrow b). One is monomer addition (oxonium exchange) and the other internal ring-closure (depolymerization). When initial monomer concentration is sufficiently low, depolymerization occurs faster than the propagation through path A for thermodynamical reasons; that is, the formation of the trans unit apparently stops. Even under this condition, the reaction through path B in Scheme II is still feasible because the cis unit 4*β* is thermodynamically more stable than the trans unit 4*α* as

Scheme II

Propagation Processes in the Polymerization of 3(e),4(a)-Bis(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane



proved by the isomerization experiment. Consequently, monomer addition to the penultimate unit 1 from the direction of the arrow b takes place to form the cis unit at the expense of the trans unit in dilute solution. The cis unit once incorporated in the polymer chain is not so readily depolymerized even if monomer concentration is low, as the reverse reaction from the oxonium ion IV to the ion I is significantly retarded because of the severe steric hindrance.

In addition, the formation of the cis unit is presumably assisted by the so-called reverse anomeric effect:[27,28] In general, tetrahydropyran derivatives possessing a positvely charged equatorial substituent at the C-2 position exist in preference to the corresponding axially substituted counterparts. If this generalization is applicable to the present system, the oxonium ion IV is supposed to be more stable than the oxonium ion I, and thus the formation of the cis unit would be more favorable.

With increasing initial monomer concentration, the monomer addition from the direction of the arrow a overcomes the depolymerization process, and the trans unit is incorporated in the polymer chain. In other words, the polymerization comes to be kinetically controlled with the increase in the initial monomer concentration.

Lowering the polymerization temperature also enhances the trans unit content in the polymer chain for the following reasons: (1) The equilibrium monomer concentration decreases as polymerization temperature is lowered. Thus, the polymerization of 3 at −78 °C gave polymers containing both the cis and trans units, even when the initial monomer concentration was low enough to yield the cis-2,6-linked polymer in the polymerization at −60 °C. (2) The polymerization at lower temperatures is governed by kinetic factors rather than thermodynamic factors, especially in the initial stage of the polymerization. The formation of the cis unit (path B in Scheme II) is kinetically disadvantageous compared to that of the trans unit because the former reaction has to pass through the relatively high-energy state III. Therefore, the polymerization at −90 °C with use of a relatively high monomer concentration and antimony pentachloride as the initiator gave the completely trans-2,6-linked polymer (number 14 in Table I). The polymerization initiated with phosphorus pentafluoride proceeded very slowly at −90 °C, and as a consequence some cis units were incorporated in the polymer chain due to the partial contribution of thermodynamic control (number 12 in Table I).

The polarities of the solvents affected the polymer structure as well. The polymerization in toluene gave the polymer having a higher trans unit content than that in dichloromethane with the same initial monomer concentration at −60 °C. It was reported that equilibrium monomer concentrations became lower in solvents of lower polarities in the cationic ring-opening polymerization of tetrahydrofuran[29] and 1,3,5-trioxane.[30] This tendency is probably valid also in the polymerization of 3. The preferential formation of the cis units takes place when the successive addition of monomer from the direction indicated by the arrow a is retarded due to the ring–chain equilibrium. Since this equilibrium should be established in more dilute solution in toluene, the trans unit tends to be formed relatively more easily in toluene than in dichloromethane.

As for the initiator effect, any significant change in the proportions of the cis and trans units was not observed among the polymers prepared with three different initiators at −60 °C under otherwise similar conditions (numbers 5–7 in Table I). This is strongly indicative of the absence of the specific counteranion effect favoring the formation of the cis unit in the polymerization of 3.

Finally, the aforementioned differences in the polymerization behavior between 3 and 5 should be briefly referred to. Although 5 bears a structural resemblance to 3, the cis-linked polymer was not obtained in the polymerization of 5. In the trialkyloxonium ion of 5 corresponding to I in Scheme II, the presence of the additional, axially oriented benzyloxy group disfavors the monomer addition to the penultimate unit from the direction of the arrow b, because the resulting ion corresponding to III is of a higher conformational energy due to its tetraaxially substituted tetrahydropyran ring. Moreover, in the polymerization of bicyclic acetals or anhydrosugars containing a tetrahydropyran ring by an S_N2 mechanism, cis vicinal substituents located on the tetrahydropyran ring experience eclipsing when the tetrahydropyran ring is flipped. Thus, 3 has a pair of substituents, whereas 5 possesses two pairs, which pass through an eclipsed state when these compounds are ring-opened in their polymerizations. Therefore, 5 cannot undergo oxonium exchange, which needs a higher energy, and the propagation takes place

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through the normal S_N2 mechanism to form the polymer exclusively consisting of the trans units **6**.

In summary, the polymerization of **3** afforded the polymers having a cis unit content varying from 0 to 100% only with slight modifications of the polymerization conditions. The formation of the cis unit was reasonably interpreted in terms of the S_N2 type propagation involving a cyclic trialkyloxonium ion accompanied by oxonium exchange at the penultimate unit of the polymer chain. In the polymerization with lower initial monomer concentrations and at higher temperatures, the polymer consisting of the cis units is predominantly formed by thermodynamic control. In the polymerization with higher initial monomer concentrations and at lower temperatures, the polymer composed of the trans units is preferentially produced under the influence of kinetic control.

Registry No. **3**, 92420-59-2; **3** (diol), 34339-25-8; **3** (homopolymer), 114377-67-2; benzyl chloride, 100-44-7.

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Equilibrium Polymerizations of 7,8-Dibenzoyl-, 7,8-Diacetyl-, and 7,8-Dibutoxycarbonyl-7,8-dicyanoquinodimethane and Their Copolymerizations with Styrene: A New Concept on the Mechanism of Alternating Copolymerization

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ABSTRACT: Kinetics of polymerization of 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ), 7,8-diacetyl-7,8-dicyanoquinodimethane (AcCQ), and 7,8-dibutoxycarbonyl-7,8-dicyanoquinodimethane (BCQ) have been studied in chloroform solutions using 2,2′-azobis(isobutyronitrile) as an initiator. These polymerizations were found to be greatly influenced by depolymerization. The ceiling temperatures and the equilibrium monomer concentrations were determined. The values of enthalpy (ΔH) and entropy changes (ΔS) of the polymerization were found to be $\Delta H = 21.6$ kJ/mol and $\Delta S = 37.5$ J/K·mol for BzCQ, $\Delta H = 25.4$ kJ/mol and $\Delta S = 36.9$ J/K·mol for AcCQ, and $\Delta H = 26.4$ kJ/mol and $\Delta S = 36.8$ J/K·mol for BCQ. These ΔS values are one-third as large as the corresponding ones (100–130 J/K·mol) for vinyl and related compounds, suggesting one of the features of polymerization of quinodimethane compounds. Their copolymerizations with styrene were carried out at various temperatures to change in copolymerization fashion from random to alternating depending upon whether these quinodimethane compounds are homopolymerizable or not, implying an influence of depolymerization. A new concept on the mechanism of radical alternating copolymerization was proposed.

Introduction

Previously it was reported that 7,8-dialkoxycarbonyl-7,8-dicyanoquinodimethanes (ACQ),[1-3] carrying two different electron-accepting substituents at each 7- and 8-position, are obtainable as stable crystal at room temperature, are homopolymerizable with free radical and anionic initiators, especially the latter of which such as butyllithium gives a high polymer with molecular weight above some millions, and are copolymerizable with styrene (St) in a random fashion. Very recently 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ)[4] and 7,8-diacetyl-7,8-dicyanoquinodimethane (AcCQ),[4] carrying electron-ac-

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