Table IV
Rate Constants at 85 °C, Activation Energy, and Lifetime at 35 °C (RH 100% for All)

material	k, 10^2 day^{-1}	k', 10^2 day^{-1}	E, kJ/mol[a]	t_L, days
67 PCL	16	24	83.3 ± 2.1	1400
71 PCL	19	27	68.0 ± 3.1	800
100 PCL	29	29	69.5	
63 PTMA	20	32	69.8 ± 1.0	600
100 PTMA	30	30	72.8	

[a] 1 kJ = 0.239 kcal.

acid contents and molecular weights in eq 1 or 2, which may then be solved for t_L:

$$t_L = \frac{\ln (A_L/A_0)}{k} = \frac{\ln [(A_0 + M_L^{-1} - M_0^{-1})/A_0]}{k} \quad (3)$$

A_0 and M_0 may be taken from Table I. Tensile measurements for the three polymers after aging suggest that M_L and A_L are about 5000 g/mol and 1.6×10^{-4} equiv/g, respectively. At 35 °C, 100% RH, values of k from the lines of Figure 5 are 0.18, 0.46, and 0.44×10^{-2} day^{-1} for polymers 67 PCL, 71 PCL, and 63 PTMA, respectively. Values of t_L in Table IV were calculated by using the above figures in eq 3. If the value of k for polymer 67 PCL is the value found experimentally, 0.11×10^{-2} day^{-1}, instead of that on the lowest line, then t_L would be about 2200 days. The exponential nature of eq 1 and 2 means that the degradation accelerates markedly with time. Consequently, the time interval between marginal usefulness and complete failure may be small. Lifetime estimates at varying temperatures and humidities should make use of a k that is appropriately weighted for the fraction of time spent in each condition.

The equations used here can be applied to lifetime estimates of filled insoluble polyester urethanes by degrading a series of samples at two or more high temperatures until the organic component is soluble at two different aging times at each temperature. After filtration, the acid content of the organic portion can be determined. The variation of A with time then gives k by eq 1, since the calculation can be done with the ratio of two acid contents and the aging time increment associated with them. The acid contents could be extrapolated backward in time to give A_0 for undegraded polymer and also an A characteristic of the limiting lifetime. This limiting lifetime probably would be judged by the physical behavior of samples degraded less extensively than those used for the acid measurements. Extrapolation of k by the Arrhenius equation would give values at the temperatures of interest. Lifetime estimates would involve the use of eq 3 with values of k, A_0, and the A characteristic of the limiting lifetime.

Acknowledgment. The authors thank Dr. Frank McCrackin and Walter J. Pummer of the National Bureau of Standards for devising the program used to calculate the molecular weights and preparing the hard segment polymer, respectively, Dr. Charles S. Schollenberger of the B. F. Goodrich Co. for describing the method used in determining the acid contents, and Charles F. Bersch and John Gurtowsky of the Naval Air Systems Command for providing the failed potting compound. The work was supported by the Office of Naval Research.

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Synthesis and Polymerization of 2,6,7-Trioxabicyclo[2.2.1]heptane and 1-Methyl-2,6,7-trioxabicyclo[2.2.1]heptane

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Received September 20, 1979

ABSTRACT: Cationic polymerizations of 2,6,7-trioxabicyclo[2.2.1]heptane (I) and 1-methyl-2,6,7-trioxabicyclo[2.2.1]heptane (VIII) were carried out under different conditions. Polymer structure was investigated by means of ^{1}H and ^{13}C NMR spectroscopy, showing that new poly(ortho esters), predominantly 2-alkoxy-1,3-dioxolane and 2-alkoxy-2-methyl-1,3-dioxane units for poly-I and poly-VIII, respectively, were formed as shown by ^{1}H and ^{13}C NMR spectroscopy. Phosphorus pentafluoride, molybdenyl acetylacetonate, and tetra-*n*-propyl titanate were very effective for the stereoselective cleavage of C_1–O_2 (and/or C_1–O_6) bonds to form five-membered rings in the polymerization of I. Poly-I prepared at 0 and 70 °C contains some units in which both rings were opened. Poly-VIII prepared at −78 °C was mainly composed of six-membered rings. If prepared at 0 °C, poly-VIII also contained some units in which both rings were opened. The analysis of the structures of poly-I and poly-VIII suggests that I and VIII are polymerized through an S_N1 mechanism with 1,3-dioxolan-2-ylium and 2-methyl-1,3-dioxan-2-ylium ions as intermediates and that the latter is more stable than the former.

To synthesize linear, stereoregular, high molecular weight analogues of the polysaccharides, bicyclic acetals have been studied by many workers.[1-9] The synthesis of stereoregular linear high polymers is an important objective for a variety of reasons mentioned in Schuerch's reviews on biomedical uses of polysaccharides.[1,2] Ring-

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opening polymerization is suitable for the synthesis of these polymers of well-defined structure. Bicyclic ortho esters also appear particularly suitable for this purpose. Kochetkov et al.[10-12] have used bicyclic ortho esters as monomers. Crank and Eastwood[13] noted that 2,7,8-trioxabicyclo[3.2.1]octane, 2,8,9-trioxabicyclo[3.3.1]nonane, and 2,8,9-trioxabicyclo[4.2.1]nonane gradually became viscous and turned to a glass at room temperature, indicating that these monomers are very easily polymerized. However, actual polymerization studies were not undertaken. Bodenbrenner[14] reported the polymerization of 1,4,6-trioxaspiro[4.4]nonane (cyclic ortho ester) but obtained a poly(ester–ether) rather than a true poly(ortho ester). W. J. Bailey et al. reported that bicyclic ortho ester (1,4-diethyl-[15] and 4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane[16]) underwent polymerization with expansion to form a polyether with ester branching and a polyester with carbonyl branching, respectively. Moreover, Bailey et al. have studied the polymerizations of spiro ortho esters,[17] ketal lactones,[18] and spiro orthocarbonates.[19]

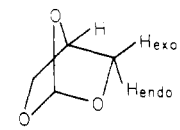
Up to date, no poly(ortho ester) of well-defined structure is known. In order to obtain basic knowledge in this field, we studied the acid-catalyzed hydrolysis of bicyclic ortho esters.[20] In this paper we report the results of the polymerization of 2,6,7-trioxabicyclo[2.2.1]heptane (I) and 1-methyl-2,6,7-trioxabicyclo[2.2.1]heptane (VIII). Synthetically and naturally, there are no known examples of poly(ortho esters), and as such, they represent a new class of polymer analogues of the polysaccharides.

Experimental Section

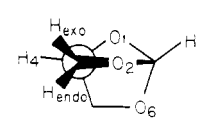
Instrumentation. ^{1}H NMR spectra were obtained using Varian-T60, Varian-XL-200, Bruker-WM-250, and Nicolet-NT-200 instruments. A Bruker WH-90 was used to obtain ^{13}C NMR spectra. Infrared spectra were recorded using Perkin-Elmer 710A and 337 spectrophotometers. Elemental analyses were performed by the University of Arizona Analytical Center (Tucson, Arizona) and Chemalytics, Inc. (Tempe, Ariz.). The number average molecular weight of polymer was determined using tetrahydrofuran or dichloroethane as solvent at 37 °C, using Hewlett-Packard vapor pressure osmometer Model 302B. Cis and trans isomers of model compounds were separated by using spinning band distillation columns (1 m and 15 cm) of the Nester and Faust Manufacturing Corp. The purity of monomers and model compounds was checked on a Varian aerograph 1700 gas chromatograph.

Materials for Monomer Synthesis and Polymerization. Glycerol was purified by distillation (bp 70–75 °C (1 mmHg)). Triethyl orthoformate was dried over calcium hydride and distilled (bp 62 °C (18 mmHg)). Trimethyl orthoacetate was purified by distillation (pb 105–107 °C). Dioctyl phthalate was dried over potassium carbonate and filtered through alumina. *p*-Toluenesulfonic acid was dehydrated by azeotropic distillation with benzene. Some benzene was distilled off, and the precipitate was recrystallized from chloroform. The anhydrous acid was dried under vacuum. Dichloromethane as a polymerization solvent was dried over calcium hydride and distilled (bp 39.5 °C). Initiators for the polymerization—methyl trifluoromethanesulfonate, boron trifluoride ethyl ether complex, trifluoromethanesulfonic acid, and trifluoroacetic acid—were purified by distillation (bp 95, 120, 162, and 72 °C, respectively). Triethyloxonium tetrafluoroborate was purifed by recrystallization, using dichloromethane and diethyl ether, respectively, as solvent and precipitator. Commercial phosphorus pentafluoride, silicon tetrafluoride, molybdenyl acetylacetonate, and tetra-*n*-propyl titanate were used without purification.

Synthesis of 2,6,7-Trioxabicyclo[2.2.1]heptane (I). Monomer I was prepared by the method outlined in the previous paper.[20] Freshly distilled anhydrous glycerol (9.2 g, 0.1 mol) and triethyl orthoformate (14.8 g, 0.1 mol) were stirred with 19 mg of *p*-toluenesulfonic acid (0.1 mmol) in 50 mL of dioctyl phthalate (DOP) in a four-necked 2-L flask at room temperature and 50 mmHg for 2 h and at 20 mmHg for 15 min. DOP, 250 mL, was



I



I'

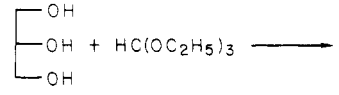
added and stirring with a Nester Faust vacuum stirrer was continued at 20 mmHg, while the temperature was gradually increased to 75 °C within 30 min. Monomer I and ethanol were collected in a receiver containing powdered potassium carbonate and chilled in liquid nitrogen. Stirring was continued at 90°C and at 0.05 mmHg for 3 h, at 110 °C and 0.05 mmHg for 3 h, and at 125 °C and 0.03 mmHg for 28 more h. Redistillation of the crude distillate from potassium carbonate, using a microspinning band column, gave pure I: 7.35 g (73%); bp 80 °C (37 mmHg), 28 °C (0.8 mmHg), and 26 °C (0.6 mmHg); ^{1}H NMR ($CDCl_3$) δ 3.64 (H_{exo} at C_3 and C_5, 2 H, d of d, $J_{H_{exo}-H_{endo}}$ = 4.9 and $J_{H_{exo}-H_4}$ = 3.2 Hz), 3.81 (H_{endo} at C_3 and C_5, 2 H, d of d, $J_{H_{endo}-H_4}$ = 1.9 Hz), 5.02 (H at C_4, 1 H, m), and 6.21 (H at C_1, 1 H, s); ^{13}C NMR ($CDCl_3$) δ 68.4 (CH_2 at C_3 and C_5), 74.3 (CH at C_4), and 110.9 (CH at C_1), the gated analysis showed that each carbon is coupled not only to the protons on their carbon, but also to the other protons, $J_{C_1-H_1}$ = 208.1, $J_{C_3-H_3}$ = 151.5, and $J_{C_4-H_4}$ = 169.1 Hz, and long-range coupling, $J_{C_1-H_4}$ = 7.4, $J_{C_4-H_1}$ = 4.4, and $J_{C_3-H_1}$ = $J_{C_3-H_{5,endo}}$ = $J_{C_5-H_{3,exo}}$ = 5.9 Hz; IR (CCl_4) 3055 and 3020 (ν_{C-H} at C_1, w), 2960 and 2880 (ν_{C-H}, m), 1490, 1475, 1360, 1335, 1305, and 1245 (δ_{C-H}), 1175 (w), 1150 (s), and 1015 (m), 965, 945, 905 (s), and 870 (w) (ν_{C-O-C}) cm^{-1}.

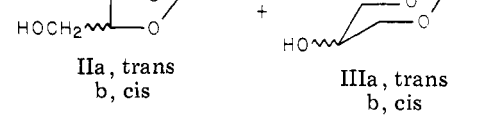
Anal. Calcd for $C_4H_6O_3$: C, 47.06; H, 5.92. Found: C, 47.00; H, 6.04.

The ^{13}C NMR spectrum shows that the $J_{C_1-H_1}$ is very large, 208.1 Hz, compared to those of 2-ethoxy-1,3-dioxolane and 2-ethoxy-1,3-dioxane (197.1 and 188.3 Hz, respectively). This shows that the s character in this C_1–H_1 bond is very high. The high frequency of the C_1–H_1 stretching vibration (3055 and 3020 cm^{-1}) in the IR spectrum supports this statement. These findings indicate that the orthoformate proton of I is unable to eliminate hydride anion as is the case with monocyclic formals.[21,22] Application of Bredt's rule also excludes possible hydride abstraction from I.

Isolation of Precursors of I as First Models for Polymer (Poly-I) Structure. Glycerol (9.2 g, 0.1 mol) and triethyl orthoformate (14.9 g, 0.1 mol) were mixed in a two-neck flask and heated to 100 °C. In a distillation apparatus, 2 mol of ethanol was distilled out of the mixture. The reaction mixture was distilled over potassium carbonate: yield, 5.2 g, 51%; bp 82–95 °C (1 mmHg).

The ^{1}H NMR spectrum showed that the distillate is a mixture of II (76%) and III (24%). The predominant precursors IIa





IIa, trans
b, cis

IIIa, trans
b, cis

(trans) and IIb (cis) were isolated by distillation over a spinning band column (1 m) in the presence of potassium carbonate: bp 46 °C (0.1 mmHg) for IIa and 46 °C (0.2 mmHg) for IIb (lit.[13] bp, none reported); ^{1}H NMR (CCl_4, 1% solution) for IIa, δ 1.18 (CH_3, 3 H, t), 1.66 (OH, 1 H, b), 3.50 (OCH_2CH_3, 2 H, q), ~3.6 (CH_2OH and CH_2 at C_5, 4 H, m), 4.3 (CH at C_4, 1 H, m), and 5.67 (CH at C_2, 1 H, s); ^{1}H NMR (CCl_4, 1% solution) for IIb, δ 1.23 (OCH_2CH_3, 3 H, t), 2.37 (OH, 1 H, d of d, J = 4.0 and 8.2 Hz), 3.57 ($-OCH_2CH_3$, 2 H, q), ~3.7 (CH_2OH, 2 H, m), 4.02 (CH_2 at C_5, 1 H, b), 3.88 (CH_2 at C_5, 1 H, d of d, J = 2.4 and 0.4 Hz), 4.2 (CH at C_4, 1 H, m), and 5.65 (CH at C_2, 1 H, s); IR (CCl_4, 1% solution) for IIa, 3600 (ν_{O-H}, free OH, m), 3490 (ν_{O-H}, hydrogen bonded OH, m), 2980, 2940, and 2890 (ν_{C-H}, m), 1480, 1450, 1400, 1375, 1350, and 1305 (δ_{C-H}, m), and 1145, 1070, and 1020 cm^{-1}

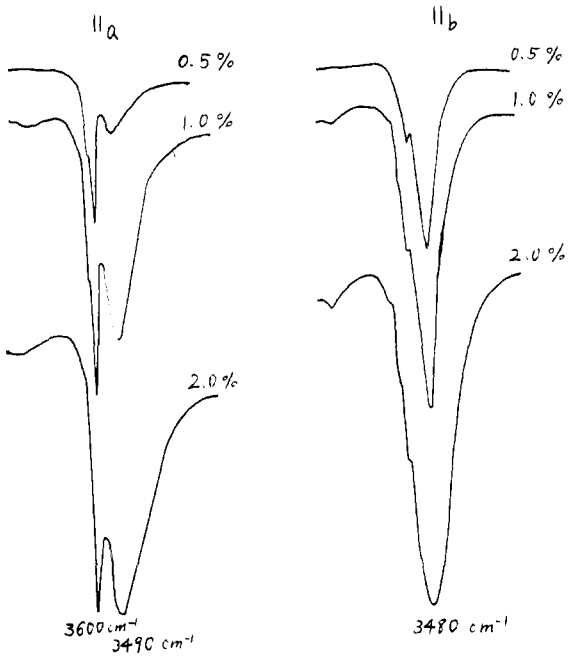


Figure 1. IR spectra of the hydroxyl group in precursors IIa and IIb (solvent, CCl_4).

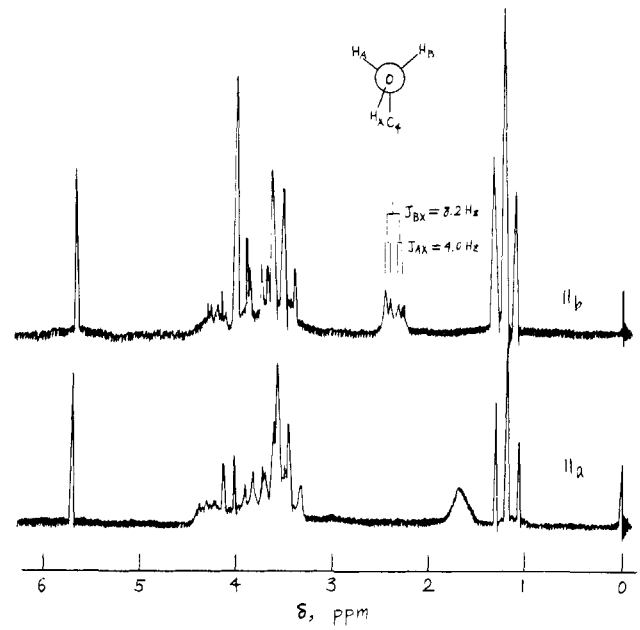
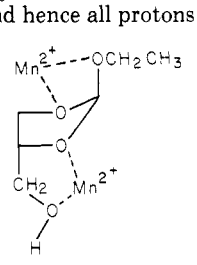


Figure 2. ^1H NMR spectra of precursors IIa and IIb (CCl_4, 1%, room temperature).

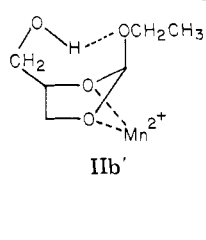
(ν_{C-O-C}, s); IR (CCl_4, 1% solution) for IIb, 3480 (ν_{O-H}, hydrogen bonded OH, m), 2980, 2935, and 2880 (ν_{C-H}, m), 1480, 1450, 1405, 1380, 1360, 1350, 1320, 1295, and 1215 (δ_{C-H}, m), and 1145, 1120, 1105, 1065, and 1005 (ν_{C-O-C}, s) cm^{-1}.

Anal. Calcd for $C_6H_{12}O_4$: C, 48.64; H, 8.16. Found: IIa, C, 47.94; H, 8.22; IIb, C, 48.04; H, 8.29.

The boiling point of IIb is the lowest of all the precursors, showing that the intramolecular hydrogen bonding of IIb is the strongest. The hydroxyl proton of IIb (cis isomer) could form a hydrogen bond with any of three oxygens (two ring oxygens and the ethoxy oxygen). From a molecular model, the distance between the hydroxyl proton and the ethoxy oxygen is the nearest of all, indicating that their hydrogen bond is the strongest, i.e., the boiling point of the cis isomer may be lower than that of the trans isomer. This finding is supported by their IR spectra (Figure 1). In the IR spectra, IIa shows two absorbances at 3600 and 3490 cm^{-1} assigned to ν_{O-H} due to free and hydrogen bonded hydroxyl groups, respectively. However, even in 0.5% solution, IIb shows only one signal (3480 cm^{-1}, ν_{O-H}, bonded). Moreover, the ^1H NMR spectrum of a <1% solution of IIb (Figure 2) shows the hydroxyl proton at δ 2.3–2.4 (q) as an ABX system, indicating that the hydroxyl group is fixed in a certain conformation, possibly because of the intramolecular hydrogen bonding between the hydroxyl proton and the ethoxy oxygen. Further, a 1% deuteriochloroform solution (1 mL) was mixed with a 10% manganese chloride solution in water (1 mL) with vigorous stirring. For both isomers the same procedure was carried out. The deuteriochloroform layers were analyzed by the ^1H NNR spectrum. However, the methylene and methyl protons of the ethoxy group in the solution containing the IIb isomer show their signals at the normal shifts without any strong line broadening. These results indicate that the IIa isomer may readily be chelated by the paramagnetic ion Mn^{2+} on both sides of the five-membered ring (IIa') and hence all protons are affected in the NMR spectrum.



IIa'



IIb'

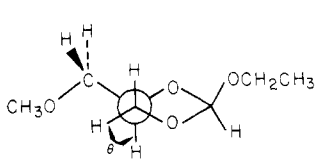
On the other hand, one side of the IIb isomer is not favorable to chelation by the ion because of the strong hydrogen bond. As a result, the methyl and methylene protons of the ethoxy group are not affected by the ion (IIb'). From all of the above results, it would be reasonable to conclude that IIa and IIb are, respectively, the trans and cis isomers. The chemical shifts of the orthoformate protons were the most useful numbers for assigning the stereochemistry of poly-I (Table I).

Synthesis of 2-Ethoxy-4-(methoxymethyl)-1,3-dioxolanes (IV) as Second Models for the Poly-I Structure. Metallic sodium (25.3 g, 1.1 mol) was dissolved in 300 mL of methanol, and the solution refluxed (64 °C). To the hot solution 110.6 g of 3-chloro-1,2-propanediol was added slowly during 0.5 h with vigorous stirring. The solution was refluxed at 76 °C for 2 h. 3-Methoxy-1,2-propanediol was distilled under reduced pressure: bp 78.5 °C (1.0 mmHg) and 68 °C (0.45 mmHg) (lit.[24] bp 110 °C (13 mmHg)); yield, 64.8 g, 61.1%.

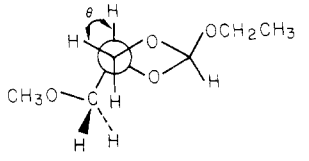
3-Methoxy-1,2-propanediol (53.1 g, 0.50 mol) was mixed with triethyl orthoformate (74.1 g, 0.50 mol). The solution was heated up to 140 °C in the presence of a small amount of *p*-toluenesulfonic acid until 1 mol of ethanol was distilled out of the solution. 2-Ethoxy-4-(methoxymethyl)-1,3-dioxolane was distilled over potassium carbonate: bp 49–52.5 °C (0.7 mmHg); yield, 59.7 g, 73.6%. The isomeric mixture was isolated into cis and trans isomers in the spinning band column in the presence of potassium carbonate: bp 50–52 °C (37 mmHg) (fraction 1) and 54 °C (4.75 mmHg) (fraction 2). Tentative assignments are fraction 1 cis and fraction 2, trans: ^1H NMR ($CDCl_3$) fraction 1, δ 1.21 (CH_3, 3 H, t, J = 7.1 Hz), 3.39 (CH_3O, 3 H, s), 3.49 ($CH_3O\mathbf{CH}_2$, 2 H, q, J = 9.9 and 5.9 Hz), 3.59 ($CH_3\mathbf{CH}_2O$, 2 H, q, J = 7.1 Hz), 3.79 (H_{endo} at C_5, 1 H, q, $J_{H_{endo}-H_{exo}}$ = 7.6 Hz and $J_{H_{endo}-H\text{ at }C_4}$ = 7.6 Hz), and 4.07 ($H_{exo\text{ at }C_5}$, 1 H, q, $J_{H_{exo}-H\text{ at }C_4}$ = 6.8 Hz), and 5.81 (CH at C_2, 1 H, s); ^1H NMR ($CDCl_3$) for fraction 2, δ 1.21 (CH_3, 3 H, t, J = 7.1 Hz), 3.39 (CH_3O, 3 H, s), 3.44 ($CH_3O\mathbf{CH}_2$, 2 H, q, J = 5.5 and 2.5 Hz), 3.59 ($CH_3\mathbf{CH}_2O$, 2 H, q, J = 7.1 Hz), 3.76 ($H_{endo\text{ at }C_5}$, 1 H, q, $J_{H_{endo}-H_{exo}}$ = 7.7 Hz and $J_{H_{endo}-H\text{ at }C_4}$ = 5.3 Hz), 4.15 ($H_{exo\text{ at }C_5}$, 1 H, q, $J_{H_{exo}-H\text{ at }C_4}$ = 7.0 Hz), and 5.85 (CH at C_2, 1 H, s); IR (CCl_4) for isomeric mixture, 2980, 2925, 2885, 2830, and 2805 (ν_{C-H}, m), 1480, 1460, 1450, 1405, 1375, 1350, 1320, 1300 (w), and 1205 (m) (δ_{C-H}), 1145 (m), 1080 (s), 1025, 1005, 970, and 960 (m) (ν_{C-O-C}), and 875 (δ_{C-H}, w) cm^{-1}.

Anal. Calcd for $C_7H_{14}O_4$: C, 51.84; H, 8.70. Found: fraction 1, C, 51.50; H, 8.79; fraction 2, C, 51.79; H, 8.73.

Fraction 1 shows $J_{H_{exo\text{ at }C_5}-H\text{ at }C_4}$ = 6.8 Hz for H–H coupling whereas fraction 2 shows $J_{H_{exo\text{ at }C_5}-H\text{ at }C_4}$ = 7.0 Hz. From the original Karplus curve it is defined that fraction 1 and 2 isomers exist in conformations wherein the cis neighboring hydrogen dihedral angles (at C_4 and C_5) are 29 and 27°, respectively. The repulsion between the ethoxy oxygen at C_2 and the methoxymethyl oxygen at C_4 in cis isomer IVa could be higher than that in IVb.



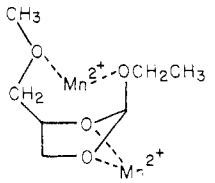
IVa, $\theta = 29°$, $\delta = 5.81$ ppm



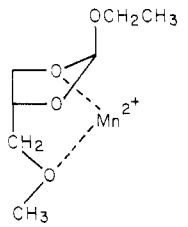
IVb, $\theta = 27°$, $\delta = 5.85$ ppm

On this basis, fraction 1 is tentatively assigned to the cis isomer and fraction 2 is assigned to the trans isomer. The repulsion affects the chemical shift of the methine at C_2, so that the methine at C_2 will be at a more pseudoaxial position in the cis isomer than the methine in the trans isomer.

In analogy with the experiment for IIa and IIb, a 1% deuteriochloroform solution (1 mL) of both isomers IVa and IVb was mixed with a 10% manganese chloride solution in water (1 mL) and the ^1H NMR spectra of the organic layers were recorded. Although all protons in fraction 1 disappeared, the ethoxy methyl and the methylene protons in fraction 2 are observed. These results show that both sides of the ring in fraction 1 are chelated (IVa') and only one side of the ring in fraction 2 is chelated by the paramagnetic ion Mn^{2+} (IVb'). This supports the above assignment.



IVa'



IVb'

Synthesis of 4-(Chloromethyl)-2-ethoxy-1,3-dioxolanes (V) as Third Models for the Poly-I Structure. Epichlorohydrin (139 g, 1.5 mol) was suspended in 200 mL of water, and 2 mL of sulfuric acid was added. The suspension was allowed to react at 100 °C for 12 h with vigorous stirring. The suspension gradually changed to a clear solution. 3-Chloro-1,2-propanediol was distilled without removal of the acid used as a catalyst for the hydrolysis: yield, 220 g, 99.5%; bp 110 °C (8.5 mmHg) (lit.[26] bp 119–119.5 °C (14.5 mmHg)).

3-Chloro-1,2-propanediol (110 g, 1.0 mol) was mixed with triethyl orthoformate (148 g, 1.0 mol), and the solution was allowed to react at 110 °C until 2 mol of ethanol distilled out of the mixture. The cis and trans isomeric mixture of V was distilled under reduced pressure: yield, 144 g, 86.5%; bp 65 °C (3.75 mmHg) and ~60 °C (1.0 mmHg) (lit.[27,28] bp 197–198 °C (760 mmHg) and 78–81 °C (12 mmHg)). The isomeric mixtures were isolated into the cis and trans isomers over the spinning band column: bp 50–53 °C (5 mmHg) (fraction 1) and 60 °C (1.0 mmHg) (fraction 2); ^1H NMR ($CDCl_3$) for fraction 1, 1.24 ($\mathbf{CH_3}CH_2O$, 3 H, t, $J = 7.0$ Hz), 3.58 (H_{exo} of $ClCH_2$ to ring, 1 H, q, $J = 10.7$ and 8.3 Hz), 3.61 ($CH_3\mathbf{CH_2}O$, 2 H, q), 3.74 (H_{endo} of $ClCH_2$ to ring, 1 H, q, $J = 10.7$ and 5.2 Hz), 3.95 (H_{endo} at C_5, 1 H, q, $J = 8.2$ and 6.2 Hz), 4.16 (H_{exo} at C_5, 1 H, q, $J = 8.2$ and 6.6 Hz), 4.35 (CH at C_4, 1 H, m), and 5.84 (CH at C_2, 1 H, s); ^1H NMR ($CDCl_3$) for fraction 2, 1.24 (CH_3, 3 H, t, $J = 7.0$ Hz), 3.47 (H_{endo} of $ClCH_2$ to ring, 1 H, q, $J = 11.0$ and 7.3 Hz), 3.59 (H_{exo} of $ClCH_2$ to ring, 1 H, q of d, $J = 11.0$, 4.8, and 0.5 Hz), 3.60 ($\mathbf{OCH_2}CH_3$, 2 H, q), 3.91 (H_{exo} at C_5, 1 H, q of d, $J = 8.3$, 4.4, and 0.4 Hz), 4.21 (H_{endo} at C_5, 1 H, q of q, $J = 8.3$, 6.6, 0.5, and 0.2 Hz), 4.52 (CH at C_4, 1 H, m), and 5.87 (CH at C_2, 1 H, s or m); IR (CCl_4) for the isomeric mixture, 2965, 2915, and 2890 (ν_{C-H}, m), 1485, 1450, 1435, 1410, 1380, 1355, 1335, 1295, and 1230 (δ_{C-H}, w), 1180, 1145, 1130 (m), 1080 (s), 1015, 980, and 965 (m) (ν_{C-O-C}), and 925 (δ_{C-H}, w) cm^{-1}.

Anal. Calcd for $C_6H_{11}O_3$: C, 43.25; H, 6.66; Cl, 21.30. Found: fraction 1, C, 43.21; H, 6.81; Cl, 21.19; fraction 2, C, 43.20; H, 6.88; Cl, 21.13.

We were unable to decide the isomers from the NMR spectra.

Synthesis of 2-Ethoxy-1,3-dioxolane (VI). 2-Ethoxy-1,3-dioxolane was prepared by the method of Mkhitaryan:[28] yield, 32.8%; bp 62 °C (30 mmHg) (lit.[28] 144–146 °C (760 mmHg)).

Synthesis of 2-Ethoxy-1,3-dioxane (VII). 2-Ethoxy-1,3-dioxane was prepared by the method of Baganz et al.:[29] yield, 30.5%; bp 78–79 °C (32 mmHg) (lit.[29] 156 °C (760 mmHg)).

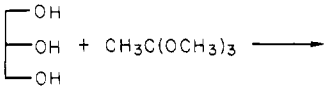
Synthesis of 1-Methyl-2,6,7-trioxabicyclo[2.2.1]heptane (VIII). Trimethyl orthoacetate (60 g, 0.5 mol) and glycerol (46 g, 0.5 mol) were mixed and heated at 100 °C until 1 mol of methanol was distilled off. The precursor was then dissolved in about 1 L of DOP and about 30 mg of *p*-toluenesulfonic acid was added. The flask was equipped with a vacuum stirrer and connected to a trap containing powdered anhydrous potassium carbonate. The trap was cooled in liquid nitrogen. The flask was heated with continued vigorous stirring to 80–100 °C for 3 h and to 130 °C for 30 h at 0.1 mmHg. VIII crystallized in the trap. A trace of triethylamine was added to stabilize the product. VIII was recrystallized several times (3 to 5) from a petroleum ether–ether mixture at −78 °C. The mother liquor could be decanted at low temperature under a nitrogen atmosphere. VIII was dried under vacuum at 0 °C and stored at −25 °C. The purity of VIII was checked by IR and NMR spectra: yield, 29.0 g, 50%; mp 26 °C. VIII is too volatile to be purified by distillation. Also, VIII is more unstable than I at room temperature. Just before use for the polymerization, VIII was purified by recrystallization (lit.[23] bp 169–170 °C (760 mmHg)): ^1H NMR ($CDCl_3$) δ 1.73 (CH_3, 3 H, s), 3.8 (CH_2 at C_3 and C_5, 4 H, m), and 4.88 (CH, 1 H, m); IR ($CHCl_3$) 3020 and 3010 (ν_{C-H}, CH_3 at C_1, w), 2970 and 2900 (ν_{C-H}, m), 1480, 1450, 1420, 1360, 1320, 1300, 1280, and 1220 (δ_{C-H}, m), 1180, 1120, 1095, and 1022 (ν_{C-O-C}, s), and 982, 950, 930, 875, 852, and 800 (δ_{C-H}) cm^{-1}.

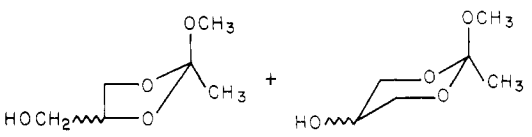
Anal. Calcd for $C_5H_8O_3$: C, 51.72; H, 6.94. Found: C, 51.66; H, 6.75.

It is very interesting that VIII also shows the stretching vibration above 3000 cm^{-1} along with the normal position (2900 and 2970 cm^{-1}) in the IR spectrum the same as I.

Isolation of Precursors of VIII as First Models for the Polymer Poly-VIII Structure. Trimethyl orthoacetate (18.0 g, 0.15 mol) and glycerol (13.8 g, 0.15 mol) were mixed together and heated to 100 °C until 0.3 mol of methanol was distilled off. The reaction product was distilled over potassium carbonate to give a mixture of IX (cis and trans) and X (cis and trans): yield, 13.6 g, 68.6%; bp 66–72 °C (0.6 mmHg); ^1H NMR ($CDCl_3$, 1% solution) δ 1.45, 1.47, and 1.60 (CH_3, 3.0 H, three singlets), 2.0 and 2.8 (OH, 0.4 and 0.6 H, respectively, b), 3.28, 3.29, 3.30, and 3.32 (OCH_3, 1.2, 1.2, 0.3, and 0.3 H, respectively, four singlets), and 3.5–4.5 (CH_2 and CH, 4.9 H, m); IR (CCl_4) 3590 (ν_{O-H}, free OH, m), 3470 (ν_{O-H}, bonded OH, m), 3000, 2945, and 2940 (ν_{C-H}, m), 1470, 1445 (w), 1400 (m), 1355, 1340 (w), and 1275 (m) (δ_{C-H}), 1200 (m), 1165, 1135, and 1055 (ν_{C-O-C}, s), and 940 (m) and 820 (s) (δ_{C-H}) cm^{-1}.

We were unable to separate this mixture by distillation in a spinning band column GC—traces were not well resolved. However, by comparing these spectra with the NMR spectra of 2-methoxy-2-methyl-1,3-dioxolane and -1,3-dioxane and 2-methoxy-4-(methoxymethyl)-2-methyl-1,3-dioxolane (see below), the signals at δ 3.28 and 3.29 are assigned to the methoxy protons in IX and the signals at δ 3.30 and 3.32 are assigned to the methoxy protons of X, showing that the precursor is composed of IX, cis; IX, trans; X, cis; and X, trans in a ratio of 1:1:4:4.

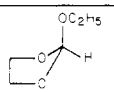
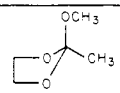
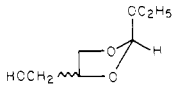
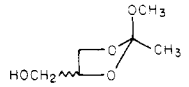
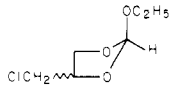
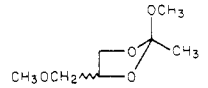
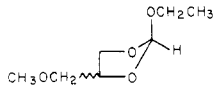
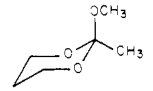
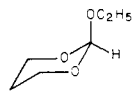
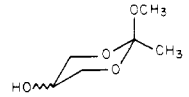
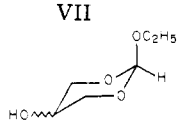
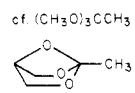
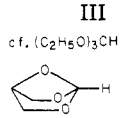




IX, cis and trans X, cis and trans

Synthesis of 2-Methoxy-4-(methoxymethyl)-2-methyl-1,3-dioxolane (XI) Isomers as Second Models for the Poly-VIII Structure. 3-Methoxy-1,2-propanediol (5.31 g, 0.05 mol) and trimethyl orthoacetate (6.01 g, 0.05 mol) were mixed together. The solution was hated to 100 °C with vigorous stirring until 0.1 mol of methanol was distilled out of the mixture. The isomeric mixture of XI was distilled over potassium carbonate: yield, 6.72

Table I
Chemical Shifts of Orthoformate and Orthoacetate Methyl and Methoxy Protons[a]

	orthoformate proton,[b] δ		orthoacetate proton, δ	
			methyl[b]	methoxy[b]
 VI	5.78	 XII	1.47	3.29
 II	IIa, trans 5.85 IIb, cis 5.82	 IX	1.60[c]	3.30 and 3.32[c]
 V	5.87 and 5.84	 XI	1.53 and 1.56	3.26 and 3.44[d]
 IV	5.85 and 5.81	 XIII	1.46	3.27
 VII	5.22	 X	1.45 and 1.47[c]	3.28 and 3.29[c]
 III	5.41 and 5.25[c]	cf. $(CH_3O)_3CCH_3$  VIII	1.43 1.73	3.24
cf. $(C_2H_5O)_3CH$  I	5.17 6.21			

[a] Solvent, $CDCl_3$, ca. 1%. [b] All signals are singlets on a 60 MHz NMR. [c] Contrary to the other compounds shown in this table, these chemical shifts were determined from the spectra of their isomeric mixtures. [d] The signal at δ 3.44 is assigned to methoxy methyl protons at C_4.

g, 82.6%; bp 40 °C (1.25 mmHg). These isomers were not separated by spinning band distillation: ^1H NMR ($CDCl_3$) δ 1.53 and 1.56 (CH_3, 3.0 H, two singlets, peak ratio, 1:1), 3.26 and 3.44 (OCH_3, 6.0 H, two singlets), and 3.4–4.6 (two OCH_2 and CH, 5.1 H, m); IR (CCl_4) 3000, 2950, 2900, and 2850 (ν_{C-H}, m), 1470 (m), 1435 (w), 1385 (m), 1330 (w), and 1245 (s) (δ_{C-H}), 1200, 1140, 1115, and 1060 (ν_{C-O-C}, s), and 950 and 890 (δ_{C-H}, m) cm^{-1}.

Anal. Calcd for $C_7H_{14}O_4$: C, 51.84; H, 8.70. Found: C, 52.03; H, 8.49.

Synthesis of 2-Methoxy-2-methyl-1,3-dioxolane (XII) and 2-Methoxy-2-methyl-1,3-dioxane (XIII). Ethylene glycol (3.10 g, 0.05 mol) and trimethylene glycol (3.80 g, 0.05 mol) were mixed with trimethyl orthoacetate (6.01 g, 0.05 mol), respectively. The solutions were heated to 100 °C until 0.1 mol of methanol was distilled out of the mixture. XII and XIII were distilled: yield, 4.23 g, 71.6% (XII); 4.08 g, 61.7% (XIII); bp 53 °C (1.2 mmHg) for XII (lit.[31,32] bp 132–134 °C (745 mmHg)); bp 75–76 °C (1.3 mmHg) for XIII. The required NMR signals for these compounds are given in Table I.

Polymerization. A typical polymerization of I was carried out as follows. Monomer (ca. 1 g, 9.79×10^{-3} mol) was weighed into a small glass ampule under argon atmosphere. The ampule was cooled in dry ice–methanol. Dichloromethane (1 or 2 mL) containing the required amount of initiator (~1 mol % to monomer) was added. The ampule was cooled at liquid nitrogen temperature, evacuated, and sealed off. The polymerization was carried out at −78 °C, 0 °C, and room temperature and terminated by the addition of 1 mL of methanol containing 20% triethylamine. The solution was poured into a large amount of methanol. The precipitate (methanol insoluble polymer) was separated by decantation, purified by reprecipitation from methanol, and dried under vacuum to constant weight. The methanol solution was concentrated under reduced pressure. The residue was dissolved in 30 mL of dichloromethane and washed twice with 10 mL of water. Some of the dichloromethane was evaporated, and the residue was poured into a large amount of *n*-pentane. The precipitate (methanol-soluble polymer) was separated by decantation, purified by reprecipitation from *n*-pentane, and dried under reduced pressure to constant weight.

The polymerization procedure for VIII is almost the same as that for I. Poly-VIII is too soluble in normal organic solvents to precipitate. After the polymerization was terminated with methanol/triethylamine (4/1 v/v), the solution was dissolved in diethyl ether and the diethyl ether-insoluble part was filtered off. The diethyl ether solution was concentrated under reduced pressure, and the residue was dried under vacuum to constant weight.

Treatment of Poly-I with Initiator. To examine the possibilities of isomerization and/or cleavage of the polymer chain after the polymerization was finished, the polymer (purified and dried) was weighed under a nitrogen atmosphere and dissolved in a few milliliters of dichloromethane. To the polymer solution, the required amount of phosphorus pentafluoride or silicon tetrachloride was added at −78 °C. The solution was cooled at liquid nitrogen temperature, evacuated, sealed off, and allowed to stand at a constant temperature (−78, 0, and 22 °C) for 48 h. The termination of the experiment and the purification of the polymer were carried out by the same method as that used in the polymerization; recovery, 91–96%. Compared to the ^1H NMR spectra of the original polymer and the repolymerization product, no isomerization from a five-membered ring to a six-membered ring (as mentioned later the original poly-I is composed of five-membered rings predominantly) was observed even at 22 °C. However, the number average molecular weight of the polymer was decreased, showing that cleavage of the polymer chain occurs even at −78 °C after the polymerization was finished.

Cleavage Reaction of Poly-I with Hydrogen Chloride. Poly-I (40 mg) was weighed into an NMR tube and dissolved in

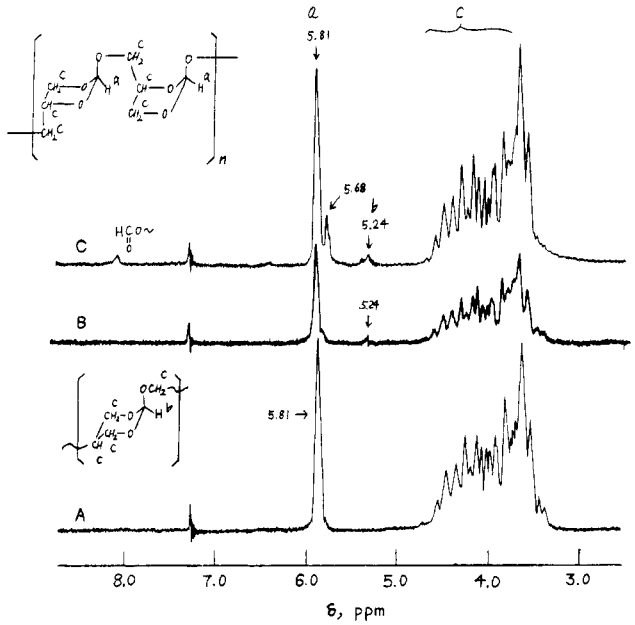


Figure 3. ^{1}H NMR spectra (60 MHz) of poly-TOH (I) (solvent, $CDCl_3$; concentration ca. 5%; room temperature): sample no. (A) 6 (MeOH insoluble fraction), (B) 8 (MeOH insoluble fraction), and (C) 5 (MeOH soluble fraction).

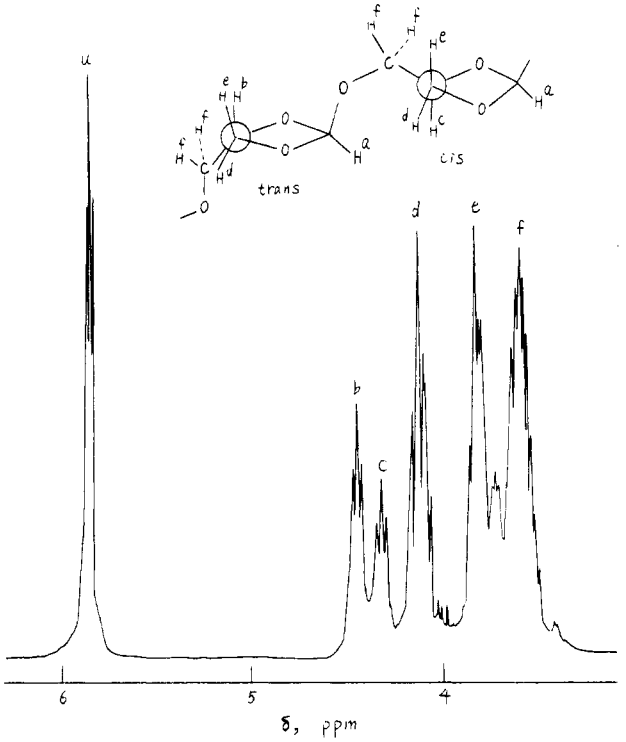
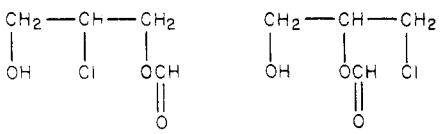


Figure 4. ^{1}H NMR spectrum (200 MHz) of poly-I (sample no. 6 (MeOH insoluble fraction); $CDCl_3$; ca. 5%).

0.50 mL of dichloromethane. Hydrogen chloride was bubbled into the solution until the orthoformate proton of the polymer disappeared. The solution was neutralized with potassium carbonate. The products were identified by means of ^{1}H NMR and IR spectroscopy: ^{1}H NMR ($CDCl_3$) δ 2.51 (OH, 1 H, s), 3.68 ($ClCH_2$ and $HOCH_2$, 3 H, m), 4.27 ($HCOOCH_2$, HOCH, and ClCH, 2 H, m), and 8.10 (HCOO, 1 H, s); IR (CCl_4) 3560 (ν_{O-H}, m), 2800–3000 (ν_{C-H}, m), 1710 ($\nu_{C=O}$, s), 1425 (m), 1340 (w), 1255 (m) (δ_{C-H}), and 1030 (m) and 1160 (s) (ν_{C-O-C}) cm^{-1}.

The relative peak area of each signal shows that the product is the equimolar mixture of XIV and XV.



XIV, 50%

XV, 50%

Results

Synthesis of Model Compounds for the Identification of Poly-I and Poly-VIII Structures. For the identification of the structures of poly-I and poly-VIII, several model compounds were synthesized. The chemical shifts of orthoformate and orthoacetate methyl and methoxy protons are summarized in Table I. From the table, orthoformate protons in five- and six-membered ring orthoformates show their signals, respectively, at 5.78–5.85 and 5.22–5.41, and the chemical shift increases with an increase of ring strain: acyclic < six-membered monocyclic < five-membered monocyclic < bicyclic ortho ester. A similar trend is observed in the chemical shifts of the methyl proton in orthoacetates, and it is shown that the differences of the chemical shift between cis and trans five-membered ring orthoformate protons and between five- and six-membered ring orthoacetate methoxy protons are very small.

Results of Polymerization of I. The results of the polymerization of I are shown in Table II. Polymer is obtained in high yield in all runs except in no. 4 and 5. The polymer is a colorless semisolid with a number average molecular weight between 3000 and 8300 for the methanol-insoluble fraction and between 1100 and 3200 for the methanol-soluble fraction. The polymer is soluble in dichloromethane, chloroform, tetrahydrofuran, and acetone and insoluble in benzene, *n*-pentane, and carbon tetrachloride.

Figure 3 shows the typical ^{1}H NMR spectra of poly-I recorded at 60 MHz along with the assignment for each signal. By comparison with the chemical shifts of orthoformate protons of authentic compounds shown in Table I, the signals at δ 5.81 and 5.24 are assigned to the orthoformate protons of five- and six-membered rings, respectively. The ratio of these two peak areas indicates the content of the five- and six-membered ring in a polymer chain. The results are shown in Table II. Every poly-I was composed almost exclusively of 1,3-dioxolane rings (five-membered ring). When phosphorus pentafluoride, molybdenyl acetylacetonate, and tetra-*n*-propyl titanate are used as an initiator, only 1,3-dioxolane rings are formed in the polymer chain (Figure 3A). The signal at δ 5.68 increases with the decrease of the number average molecular weight of the polymer, showing that the signal may be assigned to the orthoformate proton of the end units (Figure 3C). The orthoformate proton of the six-membered ring (1,3-dioxane ring) shows the signal at δ 5.24 (Figure 3B,C). The signal is very small in the polymers. The maximum content of the unit in a polymer chain is only 16% (run no. 13 in Table II).

To clarify the configuration of the polymer (cis and trans), the polymer solution was analyzed with a 200 MHz ^{1}H NMR spectrometer. Figure 4 shows the 200 MHz ^{1}H NMR spectrum of poly-I, indicating that the five-membered rings are composed of cis and trans isomers and that both isomers are random in the polymer chain. Three signals at δ 5.89_2, 5.88_0, and 5.85_9 (peak area, 1.0:1.7:1.1) may be assigned to the diads trans-trans, trans-cis and cis-trans, and cis-cis, respectively, by comparing them to the chemical shifts of the precursors IIa and IIb and the trans and cis IV and V. This finding is supported by the ^{13}C NMR spectrum (Figure 5) showing two signals at δ 115.7 and 115.3 for the orthoformate carbon of the five-membered ring. These results are very important in dis-

Table II
Polymerization of 2,6,7-Trioxabicyclo[2.2.1]heptane (I)

run no.	I, g ($\times 10^3$ mol)	initiator, mol % to I	mL of CH_2Cl_2	temp, °C	time, h	yield,[a] %	mol wt[b]	% of five-membered ring[c]
1	0.99_7 (9.76)	$CH_3OSO_2CF_3$, 1.02	1	−78	4	53.2	3000	91
						27.2	1700	99
3	0.99_7 (9.7_6)	$CH_3OSO_2CF_3$, 1.02	2	−78	20	50.6	4200	92
						27.4	1700	99
4	1.14_9 (10.2_7)	Et_3OBF_4, 0.97	1	0	4	trace		
						6.2		95
5	1.05_9 (10.3_7)	Et_3OBF_4, 0.96	2	0	48	3.2		96
						25.2	1600	91
6	0.98_7 (9.6_7)	PF_5, 0.92	2	−78	4	73.1	3300	100
						26.9	1600	100
7	0.98_4 (9.6_4)	PF_5, 0.93	2	−78	20	70.6	4100	100
						16.2	1300	100
12	0.71_7 (7.0_2)	PF_5, 0.95	2	0	48	55.6	1900	99
						35.7	1200	99
8	0.92_1 (9.0_2)	SiF_4, 0.99	2	−78	4	77.3	5700	92
						17.7	3200	94
9	0.78_2 (7.6_6)	SiF_4, 1.17	2	−78	20	74.6	3400	98
						22.2	1100	99
10	0.83_4 (8.2_6)	BF_3OEt_2, 0.95	2	−78	4	71.8	3800	96
						22.1	1800	96
11	0.91_4 (8.9_5)	BF_3OEt_2, 0.88	2	−78	20	65.0	4200	99
						28.4	1100	99
14	0.89_4 (8.7_6)	CF_3SO_3H, 1.00	2	−78	4	83.6	8300	97
						trace		
13[d]	0.98_4 (9.6_4)	BF_3OEt_2, 1.00	2	70	0.5	44.7	1600	84[e]
						16.1	1600	100
15	0.52_4 (5.1_4)	$Mo(OAcAc)_2$, 4.68	1	22	48	84.0	2900	100
						16.0	540[f]	100
16	0.50_4 (4.9_4)	$Ti(OCH_2CH_2CH_3)_4$, 4.9_6	1	22	48	0		
						100	350[f]	100

[a] Upper, methanol-insoluble polymer; lower, methanol-soluble and *n*-pentane-insoluble polymer. [b] VPO, tetrahydrofuran, 37 °C. [c] Calculated from the ^1H NMR spectra. [d] Solvent, benzene. [e] Contains 11% of formate (HCOO-) units. [f] Perhaps these polymers contain the initiator's residue.

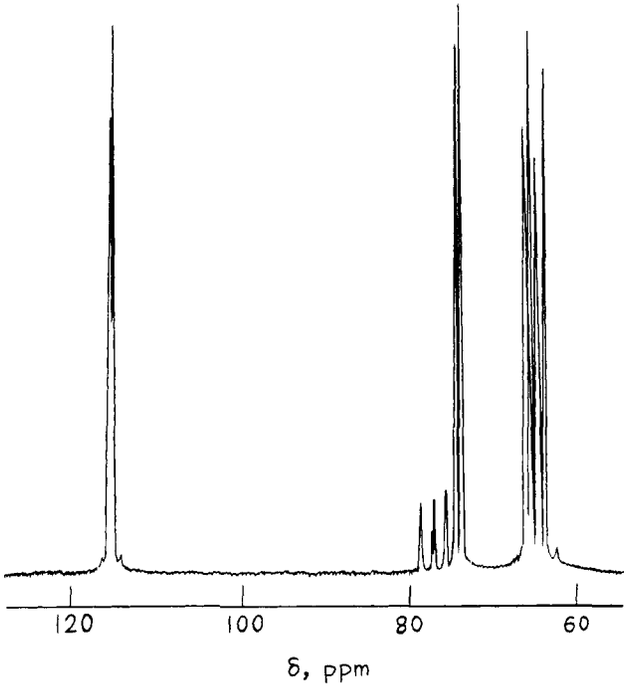


Figure 5. ^{13}C NMR spectrum of poly-TOH (I) (sample no. 6 (MeOH insoluble fraction); $CDCl_3$; 10%; room temperature).

cussing the polymerization mechanism later on.

Figure 6 (— and - - -) shows the IR spectra of poly-I. The strong absorbance at 900–1200 cm^{-1} is assigned to ν_{C-O-C}. The signals at 1300–1500 and 2800–3000 cm^{-1} are assigned to the δ_{C-H} and ν_{C-H}, respectively. The signal at 3475–3500 cm^{-1} may be assigned to the ν_{O-H} of the end group. In some

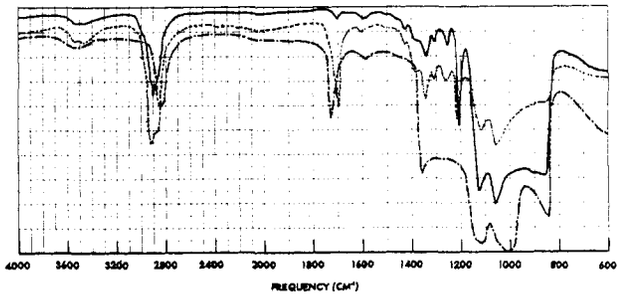


Figure 6. IR spectra of poly-TOH (— and - - -) and poly-1-Me-TOH (···): sample no. (—) 6, MeOH insoluble fraction; (- - -) 5, MeOH soluble fraction; and (···), 9.

polymers prepared at 0 and 70 °C, the absorbance at 1690 cm^{-1} is observed. The signal is assigned to the $\nu_{C=O}$ of the alkyl formate carbonyl group, which is also observed in the ^1H NMR spectrum (Figure 3C, HCOO-, δ 8.1). These results indicate isomerization of the polymer chain during the polymerization and/or the decrease of the selective reactivity of the intermediate (XIX) with the incoming monomer as mentioned in the Discussion.

Results of the Polymerization of VIII. The results of the polymerization of VIII are listed in Table III. Colorless semisolid polymer is obtained in high yield with the number average molecular weight of 2000 and 2700, significantly lower than that of poly-I. The polymer is too soluble in the normal organic solvents to precipitate.

The ^1H NMR spectrum of poly-VIII is shown in Figure 7 along with the assignment of each signal. By comparison to the model compounds shown in Table I, the signals at δ 1.48_6 and 1.49_3 are assigned to the orthoacetate methyl protons of the cis and trans six-membered ring. The two

Table III
Polymerization of 1-Methyl-2,6,7-trioxabicyclo[2.2.1]heptane (VIII)

run no.	monomer, g (mol × 10^3)	initiator, mol %	mL of solvent, CH_2Cl_2	temp, °C	time, h	yield, %	mol wt[a]	ring %[b] (six member)
1	0.106 (0.913)	Et_3OBF_4, 1	1	0	24	100		91
2	0.102 (0.879)	Et_3OBF_4, 1	1	−78	24	0		
3	0.103 (0.888)	CF_3COOH, 1	1	0	20	100		82
4	0.122 (1.05)	CF_3COOH, 1	1	−78	20	77	η_{inh} = 0.1	100
5	0.103 (0.888)	$CF_3SO_3CH_3$, 1	1	0	20	100		89
6	0.580 (5.00)	$CF_3SO_3CH_3$, 2	2.5	−78	20	100		100
7	0.492 (4.24)	CF_3SO_3H, 1	1	−78	20	100	2000	92
8	0.476 (4.10)	PF_5, 0.5	1	−78	20	9.6	2000	83
9	0.476 (4.10)	$Mo(OAcAc)_2$, 1.4	1	−78	48	100	2700	95

[a] VPO, dichloromethane, 37 °C. [b] Calculated from ^1H NMR spectra with the use of the methyl and acetate methyl protons peak area.

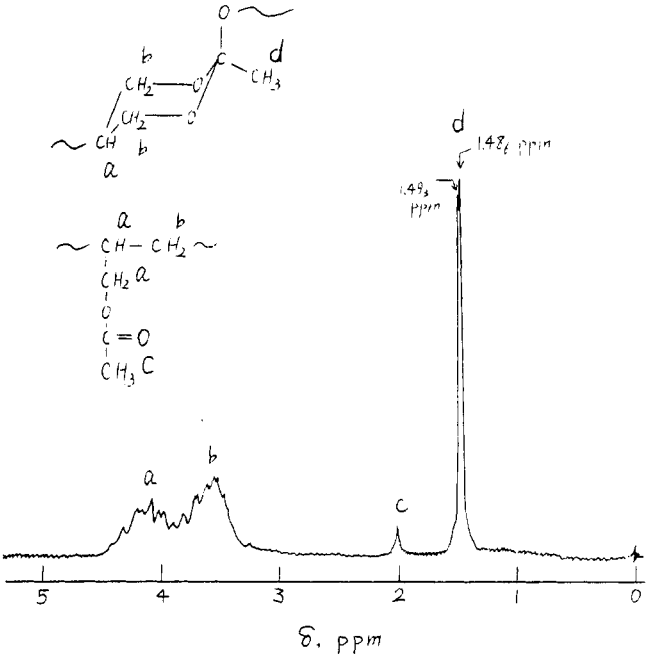


Figure 7. ^1H NMR spectrum (60 MHz) of poly-VIII ($CDCl_3$, ca. 2% solution, room temperature).

signals appear with equal intensity showing that equal amounts of cis and trans units are present, distributed randomly. The signal at δ 2.02 is assigned to acetate methyl protons which are formed by the two-ring cleavage. The signal is observed in some polymers prepared even at −78 °C, showing that the selective reactivity of the intermediate to the incoming monomer is less than that of the intermediate in the polymerization of I.

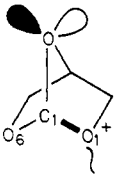
Figure 6 (- - -) shows the IR spectrum of poly-VIII. The strong absorbances at 865, 1010, and 1130 cm^{-1} are assigned to ν_{C-O-C}. The signal at 1735 cm^{-1} is due to the $\nu_{C=O}$ of the acetate substituent, showing that monomer units from which both rings have been opened are present in the polymer chain. The signal at 3500–3600 cm^{-1} is assigned to the ν_{O-H} of the end hydroxyl group.

Discussion

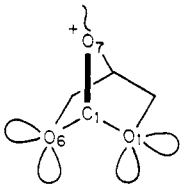
Strain in TOH (I) and 1-Me-TOH (VIII). As shown in Table II, I polymerized under different conditions to form polymers in very high yields. One case (Table I, run no. 6, time 4 h) showed 100% yield. These results indicate that the polymerization is not an equilibrium polymerization, at least not in dichloromethane at −78 °C, or that the equilibrium monomer concentration of I is very small or negligible under these conditions. This finding is due to the rigid monomer structure as mentioned in the Experimental Section. Through examination of a conventional molecular model, it was shown that I has a high ring strain. The electrons of the lone pairs on O_2, O_6, and O_7 interact with one another, and endo protons at C_3 and C_5 have a 1,3-pseudodiaxial interaction. Moreover, four p orbitals at O_2 and O_6 are situated periplanar to the methylene protons at C_3 and C_5.

Polymerization of I. Although I could potentially be opened at C_1–O_2 (and/or C_1–O_6) and C_1–O_7 bonds to form two isomeric structures of five- (1,3-dioxolane ring) and six-membered (1,3-dioxane) rings in the polymerization, in fact, the ^1H NMR spectra of polymers (Figures 3 and 4) showed that the polymers were composed predominantly of five-membered rings. For the most selective polymerization, PF_5, $Mo(OAcAc)_2$, and $Ti(OCH_2CH_2CH_3)_4$ were good initiators. Thermodynamically, the six-membered ring is more stable than the five-membered ring. The energy of the ring strain of 1,3-dioxolane and 1,3-dioxane is 7.3 and 2.9 kcal/mol,[33] respectively. Also, 1,3-dioxolane is very easily polymerized under acidic conditions,[34,35] but it is very difficult to polymerize 1,3-dioxane.[36,37] These results suggest that poly-I may be a kinetically controlled polymer.

The stereoselective control for the cleavage of the 1,2 and/or 1,6 bond is interpreted as follows: (1) The p character of lone pairs at O_2 and O_6 is higher than that at O_7 because the bond angles at the former and the latter may be near 100 and 90°, respectively. Accordingly, their nucleophilic character is also higher, so O_2 and O_6 are attacked with the initiator and the growing chain end preferentially. (2) From the stereoselective control by Deslongchamps et al.[38,39] and from the results of ab initio calculations on four selected conformations of $HOCH_2OH_2^+$ by Wipff,[40] in this polymerization, especially, one p orbital (shaded) in XVI is antiperiplanar to the C_1–O_2 (and C_1–O_6) bond to be cleaved to form a five-membered ring whereas the alternate oxonium ion XVII



XVI



XVII

has no such situation. As a result, the selective cleavage of C_1–O_2 (and/or C_1–O_6) bond occurs to form the five-membered ring in a polymer chain. For the selective cleavage of C_1–O_2 and/or C_1–O_6 bonds to form five-membered rings in the polymer, it is required that the intermediate XVIII is relatively short-lived, as implied in the

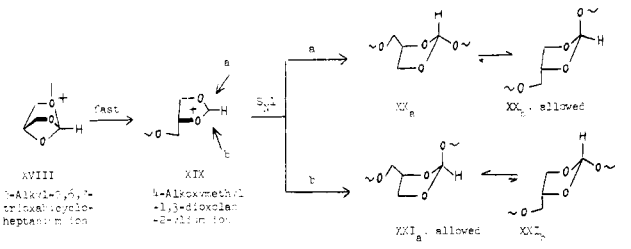


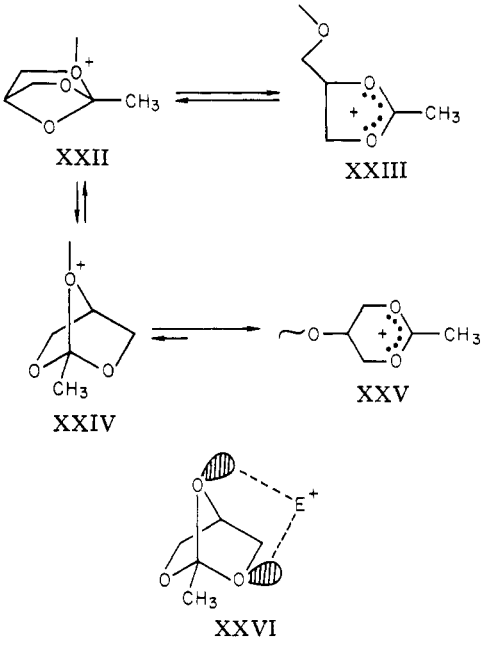
Figure 8. Polymerization scheme for poly-I.

hydrolysis of cyclic ortho esters.[39] The selective formation of a five-membered ring suggests that the polymerization of I is controlled by the stereoselective theory of Deslongchamps et al.[38,39] and that the intermediate of this polymerization is XIX. Figure 8 shows the polymerization scheme to form the five-membered ring units in the polymer chain. The growing species XIX forms both the *trans*-XX and *cis*-XXI isomers. Due to the anomeric effect,[41] XXb and XXIa are the most favorable conformations. The ^1H NMR spectrum recorded at 200 MHz (Figure 4) and the ^{13}C NMR spectrum (Figure 5) show clearly that the five-membered rings are composed of both cis and trans isomers, indicating the attacks of both a and b occurred.

Generally, the acid-catalyzed hydrolysis of ortho esters proceeds through the following three steps: (1) generation of a dialkoxy carbonium ion, (2) hydration of the ion to form a hydrogen ortho ester, and (3) cleavage of the latter to form the hydrolysis products.[42,43] Recently, it[44] has been shown by UV spectroscopy that at 25 °C the 1,3-dioxolan-2-ylium ion and hydrogen ortho ester intermediates exist in the acid-catalyzed hydrolysis of a series of 2-aryl- (and 2-cyclopropyl)-2-alkoxy-1,3-dioxolanes. Moreau et al.[45,46] reported that in the hydrolysis of 2,4,10-trioxaadamantane and 3-methyl-2,4,10-trioxaadamantane the rate-determining step is the addition of water to the corresponding carboxonium ion intermediate. Moreover, as good pseudo-first-order plots were obtained in the acid hydrolysis of I,[20] and as the oxygen adjacent to a carboxonium ion is a very strongly stabilizing group,[47,48] the intermediate XIX seems to be the more reasonable one.

In the polymers prepared at 0 and 70 °C, a formate group is observed in the ^1H NMR spectra (Figure 3C) and in the IR spectra (Figure 6B). Poly(ortho formate) (Poly-I, no. 6, methanol-insoluble fraction in Table II) is very stable in dry methanol, even at 64 °C. The same polymer is not isomerized from five- to six-membered rings in dichloromethane with phosphorus pentafluoride and silicone tetrafluoride at −78, 0, and 22 °C. From these results, it can be concluded that the formation of the formate group, HCOO, may be due to the decrease of the selective reactivity of the intermediate XIX with the attacking monomer at higher temperatures. As is the case in the polymerization of 1,4-diethyl-2,6,7-trioxabicyclo[2.2.2]octane (BF_3, 0 °C)[15] and 4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane (BF_3OEt_2, 70 °C),[16] and in analogy with the reaction of 1,3-dioxolan-2-ylium ions with weak nucleophiles (in these reactions, the thermodynamically stable compounds are formed[49]), an incoming monomer molecule will attack the intermediate XIX at C_4 and C_5 to form (formyloxymethyl)ethylene oxide and (2-formyloxy)trimethylene oxide units, respectively. However, it is very interesting that in the polymer prepared at 70 °C (Table II, no. 13) the predominant structure is the five-membered ring and the content of the formate group is only 11%.

Polymerization of VIII. Poly-VIII is mainly composed of cis and trans six-membered rings, showing that the intermediate is the 4-alkoxy-2-methyl-1,3-dioxan-2-ylium ion XXV. The situation of the lone pairs in the intermediate oxonium ions XXII and XXIV is almost the same as that in the case of I. The steric hindrance of the methyl group in the oxonium ions is also almost the same. The additional methyl may make carbenium ion XXIII sufficiently long lived to permit equilibration with XXII and XXIV as shown. Then, XXIV can undergo ring opening to the very thermodynamically stable six-ring carbenium ion XXV. Alternatively, XXII and XXIV may be reso-



nance forms of a cation XXVI, wherein the incoming electrophile coordinates simultaneously to both O_2 (or O_6) and O_7.

Conclusion

In conclusion, (1) I and VIII are very easily polymerized with acid to form poly(orthoformate) and poly(orthoacetate), respectively, and (2) in the polymerization of I, the stereoselective cleavage of the C_1–O_2 (and/or C_1–O_6) bond occurs preferentially to form five-membered (1,3-dioxolane) rings in the polymer. In particular, when phosphorus pentafluoride, molybdenyl acetylacetonate, and tetra-*n*-propyl titanate are used as an initiator, only 1,3-dioxolane rings are formed. (3) The polymers prepared at higher temperatures (0 and 70 °C) contain two ring-opened monomer units with the formate substituent, but the structure is a minor one. (4) No isomerization (from five- to six-membered rings) of the polymer chain of poly(orthoformate) I was observed in the presence of phosphorus pentafluoride and silicone tetrafluoride at −78, 0, and 22 °C. (5) Poly-I is stable in hot methanol (64 °C). (6) Poly-I (orthoformate) is very easily acid hydrolyzed with hydrogen chloride to form the corresponding formate derivatives. (7) Poly-VIII is predominantly composed of six-membered rings (1,3-dioxane rings) and (8) the monomer unit with the acetate substituent in poly-VIII is a minor structure, but the content is higher than that in Poly-I.

Finally, the object of the present work is to synthesize linear, stereoregular, high molecular weight polymer analogues to the polysaccharides. In this work only stereoselective cleavage of the C_1–O_2 (and/or C_1–O_6) bond in the polymerization of I satisfies part of the objective. Up to now there have been only a few studies on poly(ortho esters). In order to obtain basic knowledge in this field,

we hope to synthesize many more poly(ortho esters) and to study their structures and properties.

Acknowledgment. The authors are deeply indebted to the National Institutes of Health, Grant GM 18595, for support of this work and gratefully acknowledge Dr. M. Barfield for the 200 MHz NMR spectra and helpful discussion.

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