rated in the main chain, are defined here as "classical" urea type polymers. The terminology "nonclassical" is used in this series of papers in order to avoid any confusion between the familar "polyureas" and our N-substituted polyethylenimines.

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Macrocyclic Formals. 3. Two-Stage Polymerization of 1,3-Dioxacycloalkanes

Yuhsuke Kawakami and Yuya Yamashita*

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan. *Received February 14, 1977*

ABSTRACT: 1,3-Dioxacycloalkanes were found to polymerize in two stages forming cyclic oligomers in the first stage and mainly high polymers in the second stage with boron trifluoride ether complex as an initiator. Some of the formed cyclic oligomers were isolated and identified. High-speed liquid chromatography was used to obtain product distribution and preparative chromatography was also used.

There have been extensive works on the polymerization of 1,3-dioxolane. Mainly four kinds of reaction mechanism have been proposed, namely, carboxonium ion,[1] tertiary oxonium ion,[2] macrocyclic secondary oxonium ion,[3] and polymer complexed tertiary oxonium ion[4] mechanisms. There are some evidences for each mechanism but they are not always consistent to each other. We have been interested in the polymerization of cyclic formals.[1a,5–7] We proposed the carboxonium ion mechanism. Recently, we and Black and Worsfold independently reported the two-stage polymerization of 1,3-dioxacycloalkanes.[8–10] We reported that 1,3,6,9-tetraoxacycloundecane is polymerized in two stages initiated with boron trifluoride ether complex forming cyclic oligomers in the first stage and high polymers in the second stage. Black and Worsfold reported that 1,3-dioxolane is polymerized by two different mechanisms operating at the same time giving low molecular weight material and high polymers with triethyloxonium hexafluorophosphate as an initiator. Although the reaction conditions employed are different, the results seem to be very similar in the sense of two-stage character of monomer consumption. In the two-stage polymerization of 1,3-dioxacycloalkanes, the products can be separated by liquid chromatography and the information on reaction mechanism can be derived by studying the structure and amount of the products. In order to establish the two-stage character of the polymerization of 1,3-dioxacycloalkanes, the polymerizations of 1,3-dioxolane, 1,3-dioxacyclooctane, 1,3,6-trioxacyclooctane, 1,3,6,9,12-pentaoxacyclotetradecane, and 1,3,6,9,12,15-hexaoxacycloheptadecane were studied using boron trifluoride ether complex as an initiator. The polymerizations were found to proceed in two stages in all cases. The results on 1,3-dioxolane are very important, which may reflect the true reaction mechanism of the polymerization of 1,3-dioxolane.

Experimental Section

Dichloromethane and boron trifluoride ether complex were distilled under nitrogen. 1,3-Dioxacyclooctane, 1,3,6-trioxacyclooctane, 1,3,6,9,12-pentaoxacyclotetradecane, and 1,3,6,9,12,15-hexaoxacycloheptadecane were synthesized from the corresponding glycols and paraformaldehyde using *p*-toluenesulfonic acid as catalyst by a method similar to one in the literature.[11] They were dried and purified by distillation over lithium aluminum hydride four times. 1,3-Dioxolane was distilled over calcium hydride followed by distillation over lithium aluminum hydride. The purity of the dioxacycloalkanes was shown to be better than 99.9% by gas chromatography. The reaction was carried out by adding boron trifluoride ether complex to a dichloromethane solution of 1,3-dioxacycloalkane in a one-necked flask fitted with a three-way stopcock capped with a serum cap. The reaction was stopped by adding an excess amount of triethylamine. The consumption of monomer was monitored by gas chromatography on the sample pulled out from the system with a syringe through the serum cap. The gas chromatograph used in the experiment is Hitachi Model K53 connected with 1 m of column packed with Silicone GE SE-30 and FID detector was used. The product distribution was recorded on Toyo Soda high-speed liquid chromatograph Model HLC 802 UR connected with 2 m of TSK-GEL G2000 H8 (exclusion limit 2.5×10^2 Å, TP/F 8000) columns and 1 m of TSK-GEL G4000 H8 (exclusion limit 1×10^4 Å, TP/F 8000) column (Toyo Soda) unless otherwise noted. The detector for gel chromatography is a differential refractometer. The solvent is chloroform and the flow rate is 1 mL/min at 35 °C. Three counts approximately correspond to 2 mL of elution volume. The higher count number indicates the lower molecular weight.

Results

Typical examples of the time–conversion relationship of 1,3-dioxacycloalkanes initiated with boron trifluoride ether complex in dichloromethane, obtained by plotting the disappearance of monomer against time, are shown in Figure 1. Together with the results on gel chromatography which are shown in Figures 2–5, the monomer seems to be consumed in two stages forming cyclic oligomers in the first stage and high polymers in the second stage. For instance, the consumption of 1,3,6,9,12-pentaoxacyclotetradecane seems to be one stage in Figure 1 because the reaction is fast; however, in the earlier stage only cyclic oligomers are formed and mainly high polymers are formed in the latter stage of the polymerization as is reported.[12] The gel chromatogram indicates that oligomers are formed during the first relatively slow stage and high

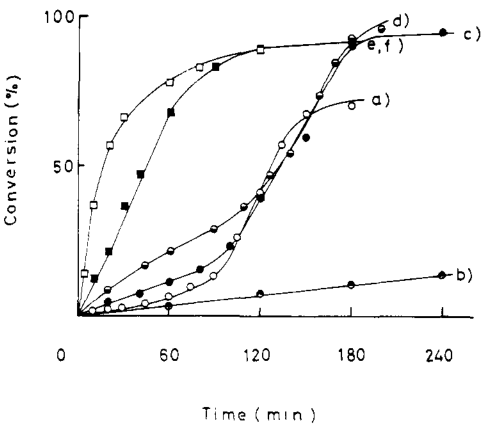

Figure 1. Time-conversion relationship of 1,3-dioxacycloalkanes (0 °C) in dichloromethane by $BF_3{\cdot}OEt_2$: $[BF_3{\cdot}OEt_2] = 1.20 \times 10^{-2}$ M; (a) ○ [1,3-dioxolane] = 3.77 M; (b) ◐ [1,3-dioxacyclooctane] = 5.0×10^{-1} M; (c) ● [1,3,6-trioxacyclooctane] = 5.29×10^{-1} M; (d) ◒ [1,3,6,9-tetraoxacycloundecane] = 4.40×10^{-1} M; (e) □ [1,3,6,9,12-pentaoxacyclotetradecane] = 5.29×10^{-1} M; (f) ■ [1,3,6,9,12,15-hexaoxacycloheptadecane] = 6.33×10^{-1} M.

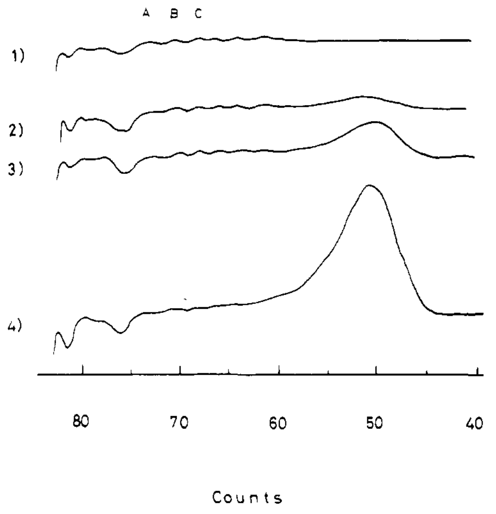

Figure 2. Gel chromatogram of the polymerization of 1,3-dioxolane as a function of reaction time. 0 °C in dichloromethane: $[BF_3{\cdot}OEt_2] = 1.20 \times 10^{-2}$ M, [1,3-dioxolane] = 3.77 M, (1) 60 min, (2) 90 min, (3) 105 min, (4) 180 min.

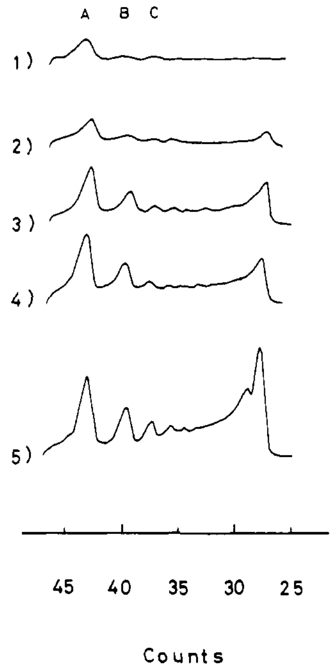

Figure 3. Gel chromatogram (2 m of G2000 H8 columns were used) of the polymerization of 1,3-dioxacyclooctane. 0 °C in dichloromethane: $[BF_3{\cdot}OEt_2] = 1.20 \times 10^{-2}$ M, [1,3-dioxacyclooctane] = 5.0×10^{-1} M, (1) 60 min, (2) 120 min, (3) 180 min, (4) 480 min, (5) 46 h.

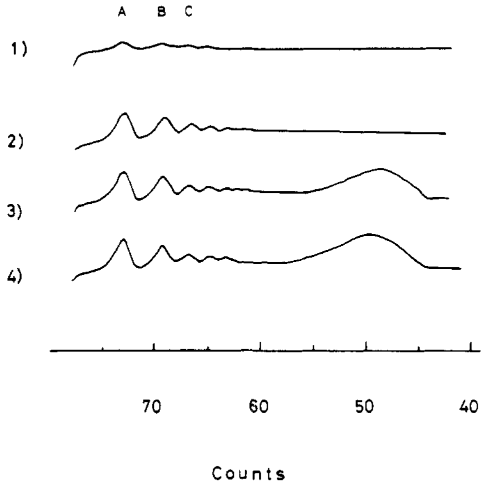

Figure 4. Gel chromatogram of the polymerization of 1,3,6-trioxacyclooctane. 0 °C in dichloromethane: $[BF_3{\cdot}OEt_2] = 1.20 \times 10^{-2}$ M, [1,3,6-trioxacyclooctane] = 5.29×10^{-1} M, (1) 60 min, (2) 90 min, (3) 120 min, (4) 180 min.

polymers are mainly formed during the second stage. The rate of the formation of oligomers was affected very much by the amount of contaminated water in the system.[6,12] Contrary to this, the rate of formation of high polymers was scarcely affected by the amount of water. Thus, the order of the reaction rate in Figure 1 may not be the true one because the amount of contaminated water in each monomer is not necessarily the same. The gel chromatograms of the reaction system are shown in Figures 2–5 for 1,3-dioxolane, 1,3-dioxacyclooctane, 1,3,6-trioxacyclooctane, and 1,3,6,9,12,15-hexaoxacycloheptadecane. A and B in Figures 2, 3, 4, and 5 correspond to the cyclic dimer and trimer of respective monomer. The molecular weight of oligomers which can be separated on these columns covers from several thousands to about one hundred. And the molecular weight of the polymer is about 2×10^4 based on polystyrene. Cyclic oligomers are formed in the first stage and high polymers are formed in the second stage for all the 1,3-dioxacycloalkanes except 1,3-dioxacyclooctane. For instance, 1,3,6-trioxacyclooctane is consumed relatively slowly until the reaction time of 90 min and faster thereafter, in Figure 1. Correspondingly to this, in the gel chromatogram in Figure 4, only the cyclic oligomers are formed with the reaction time shorter than 90 min (curves 1 and 2) and high polymers are mainly formed with the longer reaction time (curves 3 and 4). In the case of 1,3-dioxacyclooctane, cyclic dimer was first formed and all sizes of cyclic oligomers and high polymers are formed competitively. The molecular weight of polymer does not seem to change with reaction time. The molecular weight of the peak of polymer is about 10^4 based on polystyrene. The higher molecular weight cyclic oligomers were formed with the longer reaction time. This is well shown in the gel chromatogram in Figure 3. A, B, and C in Figure 3 are cyclic dimer, trimer, and tetramer of 1,3-dioxacyclooctane. After 46 h, the molecular weight of some of the oligomers reached to the region of the molecular weight of high polymers which were formed competitively with cyclic oligomers. This may be a good evidence that there are two different active species for the formation of cyclic oligomers and high polymers. Some of

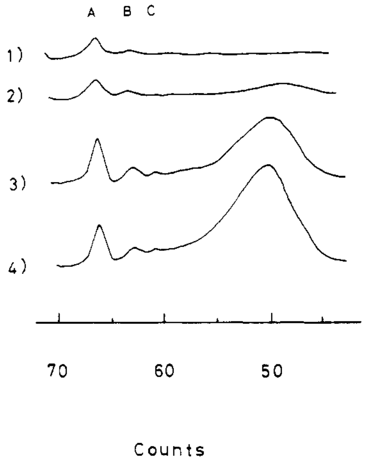

Figure 5. Gel chromatogram of the polymerization of 1,3,6,9,12,15-hexaoxacycloheptadecane. 0 °C in dichloromethane: $[BF_3 OEt_2] = 1.20 \times 10^{-2}$ M, [1,3,6,9,12,15-hexaoxacycloheptadecane] $= 6.33 \times 10^{-1}$ M, (1) 10 min, (2) 20 min, (3) 30 min, (4) 120 min.

the oligomers formed were isolated and identified (see below).

Cyclic Oligomers of 1,3-Dioxolane.[13] 1,3-Dioxolane (200 g) was polymerized by trifluoromethanesulfonic acid as an initiator and stopped with excess triethylamine. The resulting system was dissolved in 100 mL of dichloromethane and poured into 1000 mL of methanol. The supernatant solution was separated by decantation. This procedure was repeated for three times. The combined solution was evaporated on a rotary evaporator and the resulting oil was put in a sublimator. The compound sublimed at the bath temperature 100 °C under vacuum was collected and recrystallized from ethyl ether. This compound was identified as cyclic dimer of 1,3-dioxolane by mass spectrum, NMR spectrum, and elementary analysis. Calcd for $(C_3H_6O_2)_2$: C, 48.63; H, 8.17; M + 148. Found: C, 48.65; H, 8.20. Mp 67 °C; NMR ($CDCl_3$) δ 3.90 (s, 8 H), 4.83 (s, 4 H); yield 0.11 g.

The reaction products of the polymerization system in dichloromethane by boron trifluoride ether complex were separated by preparative gel chromatography. The cyclic dimer was identified by comparing its spectra and melting point with authentic sample. The cyclic trimer, tetramer, and pentamer were also identified. Calcd for $(C_3H_6O_2)_3$: C, 48.63; H, 8.17. Trimer Found: C, 48.66; H, 8.18. NMR ($CDCl_3$) δ 3.80 (s, 12 H), 4.77 (s, 6 H). Calcd for $(C_3H_6O_2)_5$: C, 48.63; H, 8.17. Tetramer Found: C, 48.65; H, 8.21. NMR ($CDCl_3$) δ 3.79 (s, 16 H), 4.77 (s, 8 H). Calcd for $(C_3H_6O_2)_5$: C, 48.63; H, 8.17. Pentamer Mp 28 °C. Found: C, 48.61, H, 8.22. NMR ($CDCl_3$) δ 3.76 (s, 20 H), 4.77 (s, 10 H).

Cyclic Oligomers of 1,3-Dioxacyclooctane. The polymerized system starting from 11.6 g of monomer was terminated with excess triethylamine. The mixture was distilled under reduced pressure until the unreacted monomer was completely distilled off, and the remaining oil was crystallized from ethanol. The crude crystal was recrystallized from a small amount of ethanol. This crystal (A in Figure 3) was identified to be the cyclic dimer of 1,3-dioxacyclooctane by comparing the melting point[13] and by the NMR spectrum. Mp 55.5 °C; NMR ($CDCl_3$) δ 1.63 (12 H), 3.66 (8 H), 4.70 (s, 4 H); Yield 0.2 g. The higher molecular weight oligomers were assumed to be cyclic because the mixture of oligomers did not show any indication having terminal groups in IR and NMR spectra.

Cyclic Oligomers of 1,3,6-Trioxacyclooctane. To the polymerized system started from 13 g of monomer which was terminated with excess triethylamine, 100 mL of benzene was added and the solution was poured into 1000 mL of *n*-hexane. The supernatant solution was separated by decantation. This procedure was repeated three times. The combined solution was evaporated to an oil. The compound, sublimed from this oil at the bath temperature 100 °C under vacuum after the complete removal of unreacted monomer, was purified by recrystallization from *n*-hexane or sublimation at 60 °C under vacuum. This compound (A in Figure 4) was identified to be the cyclic dimer of 1,3,6-trioxacyclooctane by mass spectrum, NMR spectrum, and elementary analysis. Calcd for $(C_5H_{10}O_3)_2$: formula wt 236.27; C, 50.81; H, 8.54. Mp 55 °C. Found: C, 50.83; H, 8.56. NMR ($CDCl_3$) δ 3.73, 3.77 (two s, 16 H), 4.73 (s, 4 H); M + 236. There was no detectable amount of OH in IR and NMR spectra. The cyclic trimer and tetramer were separated by preparative gel chromatography. Calcd for $(C_5H_{10}O_3)_3$: C, 50.81; H, 8.54. Trimer Found: C, 50.81; H, 8.57. NMR ($CDCl_3$) δ 3.70 (s, 24 H), 4.75 (s, 6 H). Calcd for $(C_5H_{10}O_3)_4$: C, 50.81, H, 8.54. Tetramer Found: C, 50.79; H, 8.58. NMR ($CDCl_3$) δ 3.71 (s, 32 H), 4.76 (s, 8 H). There was no indication of any terminal group in IR and NMR spectra.

Cyclic oligomers of 1,3,6,9-tetraoxacycloundecane have been reported.[8] The separation of cyclic oligomers of 1,3,6,9,12-pentaoxacyclotetradecane and 1,3,6,9,12,15-hexaoxacycloheptadecane are now in progress.

Thus all the oligomers formed in the polymerization of 1,3-dioxacycloalkanes were proved to be cyclic. The amounts of cyclic oligomers formed are shown in Table I.

The polymerization of 1,3-dioxacycloalkanes was confirmed to proceed in two stages forming cyclic oligomers in the first stage and mainly high polymers in the second stage.

Table I
Concentration of Cyclic Oligomers ($\times 10^2$ M) at 0 °C in Dichloromethane[b]

Monomer[a]	Dimer	Trimer	Tetramer	Pentamer
1,3-Dioxolane	1.9	2.0	1.8	1.2
1,3-Dioxacyclooctane	2.7	1.1		
1,3,6-Trioxacyclooctane	2.7	1.4	0.7	
1,3,6,9-Tetraoxacyclo-undecane	2.5	1.0	0.6	

[a] Initial concentration is about 5×10^{-1} M except for 1,3-dioxolane. Initial concentration of 1,3-dioxolane is 3.77 M. [b] 1.20×10^{-2} M of boron trifluoride ether complex was used as a catalyst and the reaction time is 24 h.

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