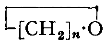
111. *Cationic Polymerisation of Oxacyclobutanes. Part I.*

By J. B. ROSE.

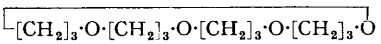
The cationic polymerisation of oxa*cyclo*butane to a mixture of a linear polyether and a cyclic tetramer is described. The effects of temperature on this reaction are reported and discussed. 3 : 3-Dimethyloxa*cyclo*butane polymerised to a mixture of polymer and tetramer, but 2-methyloxa*cyclo*butane gave only linear polymer. The polymers of oxa*cyclo*butane and its 3 : 3-dimethyl analogue are crystalline, but poly-2-methyloxa*cyclo*butane is amorphous.

SEVERAL examples of the cationic polymerisation of cyclic ethers (I) to linear polyethers having the repeating unit $\cdot[CH_2]_n\cdot O\cdot$ have been reported. Staudinger and Lehmann [1] have investigated the stannic chloride-catalysed polymerisation of ethylene oxide, and the cationic polymerisation of tetrahydrofuran, discovered by Meerwein,[2] has been described by other German workers.[3] Delfs [3] states that oxa*cyclo*butane reacts in the same way, but does not give details, and Farthing and Reynolds [4] have described the polymerisation of 3 : 3-bischloromethyloxa*cyclo*butane, which is catalysed by boron trifluoride. Only linear polymers of oxa*cyclo*butanes have been reported. The present work was undertaken to investigate the polymerisation of several oxa*cyclo*butanes, for which no detailed information was available.

Oxa*cyclo*butane polymerised on addition of catalytic quantities of boron trifluoride, the experimental method being such that adventitious water was excluded as far as possible from the system. The product was a mixture of a crystalline polyether of high molecular weight (m. p. *ca.* 35°), and a tetramer, $(C_3H_6O)_4$, which melted sharply at 70°. The infra-red absorption spectrum of the tetramer contained a strong band at 1120—1130 cm.$^{-1}$ characteristic of a strainless ether linkage, but no bands characteristic of hydroxyl, carbonyl, or $>C=C<$ groups were present. There was no absorption band at 1378 cm.$^{-1}$ where a terminal methyl group would be expected to absorb. 1 : 3-Dichloropropane was the only compound isolated (in 50% yield) from the reaction of the tetramer with hydrochloric acid at 100°. These data are consistent with the tetramer's having the structure (II).

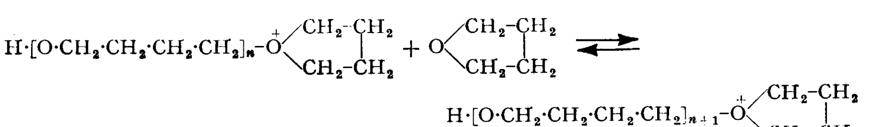
(I) 

$[CH_2]_n\cdot O$

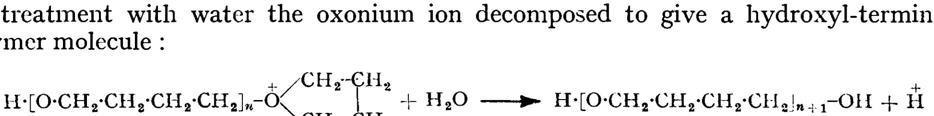
 (II)

$[CH_2]_3\cdot O\cdot[CH_2]_3\cdot O\cdot[CH_2]_3\cdot O\cdot[CH_2]_3\cdot O$

Delfs [3] considered that the polymerisation of tetrahydrofuran proceeded *via* a tertiary oxonium ion, and formulated polymerisation and depolymerisation as follows :



On treatment with water the oxonium ion decomposed to give a hydroxyl-terminated polymer molecule :



Oxa*cyclo*butane being assumed to react by a similar mechanism, a 16-membered ring could be formed by reaction of the oxonium ion with the appropriate ether linkage in the polymer chain. No homologues of the tetramer could be isolated, indicating that, in this polymerisation, a 16-membered ring is formed more readily than any other ring.

---

[1] Staudinger and Lehmann, *Annalen*, 1933, **505**, 41.
[2] Meerwein, G.P. 741,478.
[3] Delfs, Microfilm F.D. 156/48, Leverkusen 13th Oct., 1941; Hamann, *Angew. Chem.*, 1951, **63**, 231.
[4] Farthing and Reynolds, *J. Polymer Sci.*, 1954, **12**, 503; Farthing, *J.*, 1955, 3648.

The effect of temperature on the polymerisation of oxa*cyclo*butane is illustrated in Table 1. An increase in temperature increases the proportion in which the reaction yields tetramer, but decreases both the molecular weight of the polymer, and the ultimate conversion of monomer into polymer and tetramer. Delfs[3] states that an equilibrium between monomer and polymer is established during the polymerisation of tetrahydrofuran, and it has been shown[5] that the equilibrium concentration of monomer increases with temperature. However, it is apparent from the last experiment in Table 1 that, in the case of oxa*cyclo*butane, the decrease in percentage conversion brought about by an increase in temperature is not an equilibrium phenomenon. This effect may be due to the destruction of the catalyst at the higher temperature by side reactions. Theoretically it is unlikely that the polymerisation would be reversible under these conditions, for it has been estimated[6] that the free energy change of the (hypothetical) polymerisation of a liquid *cyclo*alkane at 25° to polymethylene is $-21{\cdot}5$ kcal. mole^{-1} for *cyclo*butane, but only $-2{\cdot}2$ kcal. mole^{-1} for *cyclo*pentane. Small[7] has indicated that substitution of one methylene group in the *cyclo*alkane by an oxygen atom would affect these figures only slightly, and on this basis there would be *ca.* 2% of tetrahydrofuran in equilibrium with its polymer (at 25°) but the equilibrium concentration of oxa*cyclo*butane would be very small.

TABLE 1. *Polymerisation of oxa*cyclo*butane catalysed by boron trifluoride.*

($[BF_3] = 0{\cdot}010$ mole l.$^{-1}$)

Temp	Reaction time (days)	Conversion (%)	Proportion of tetramer (%)	$[\eta]$ (dl. g.$^{-1}$)	Temp.	Reaction time (days)	Conversion (%)	Proportion of tetramer (%)	$[\eta]$ (dl. g.$^{-1}$)
−80°	14	85	4	2·9	50°	28	62	62	1·1
−80	28	95	4	2·6	50 *	14	78	65	0·8
−80 *	14	92	5	2·1	100	7	29	63	1·6
0	14	94	10	2·1	100	14	37	68	—
0 *	14	98	9	1·7	100	28	31	60	—
50	7	62	58	1·1	21 days at −80°, then				
50	14	64	66	1·3	28 days at 100°		89	6	1·6

* In these experiments the monomer was diluted with its own volume of ethyl chloride. In the other experiments the monomer was not diluted.

Boron trifluoride dihydrate also catalysed the polymerisation of oxa*cyclo*butane, but the rates were slow and the polymers were of low molecular weight. When mixtures of water with boron trifluoride were used, erratic results were obtained and in several cases explosions resulted. The effect of added water has been investigated in greater detail and is reported in Part II.[8]

3 : 3-Dimethyloxa*cyclo*butane polymerised in the presence of boron trifluoride dihydrate to give a mixture of a crystalline polymer of low molecular weight (m. p. *ca.* 45°) and a tetramer of m. p. 157° whose infrared absorption spectrum was similar to that of the tetramer prepared from oxa*cyclo*butane, and indicated the absence of all functional groups other than the ether group. Attempts to split the molecule with hydrochloric acid at 100° were unsuccessful, the tetramer being recovered unchanged. However, if the structure of this tetramer is analogous to structure (II) then the steric hindrance afforded by the methyl groups attached to the β-carbon atoms would increase the resistance of the ether linkages to hydrolysis.

2-Methyloxa*cyclo*butane polymerised in the presence of boron trifluoride ($[BF_3] = 0{\cdot}10$ mole l.$^{-1}$), but the polymer, which was of high molecular weight ($[\eta] = 2{\cdot}9$ dl. g.$^{-1}$), was amorphous. Oxa*cyclo*butane and its 3 : 3-dimethyl derivative are symmetrical molecules and can therefore give polymers of regular structure. Poly-2-methyloxa*cyclo*butane, however, should have an irregular structure, for the monomer contains an asymmetric carbon atom, and monomer can add to the growing chain to form a di-primary ($\cdot CH_2\cdot O\cdot CH_2\cdot$),

---

[5] L. S. Rayner, personal communication.

[6] Dainton, Devlin, and Small, *Trans. Faraday Soc.*, in the press.

[7] Small, *ibid.*, in the press.

[8] Rose, following paper.

a primary-secondary ($\cdot CH_2\cdot O\cdot CHMe\cdot$), or a di-secondary ($\cdot CHMe\cdot O\cdot CHMe\cdot$) ether linkage. Thus the state, either crystalline or amorphous, of these polymers can be correlated with their structures, for it is generally accepted that a polymer must possess a considerable degree of structural regularity if it is to crystallise. Oxa*cyclo*butane and its 2-methyl derivative form copolymers which, as expected, are amorphous.

EXPERIMENTAL

Microanalyses and molecular-weight determinations were carried out in the Analytical Department of this Division.

Preparation of Monomers.—(a) *Oxa*cyclo*butane.* 1-Acetoxy-3-chloropropane was prepared by a modification of Bogert and Slocum's method.[9] These authors claimed that high yields were obtained when equimolar quantities of acetyl chloride and propane-1 : 3-diol reacted in a Carius tube, and were then heated to 100° for 8 hr. However, repetition of this procedure, followed by fractionation of the product, showed that a mixture of all the possible substitution products was obtained, the principal components of which were 3-chloropropanol and 1-acetoxy-3-chloropropane. An indication of what occurs in the sealed tube, after the initial reaction, was obtained from measurements of the concentrations of chloride and acetate ions that were extracted from the product by shaking it with water (Table 2).

TABLE 2. *Reaction of acetyl chloride with propane*-1 : 3-*diol.*

Time of heating at 100° (hr.)	0	2	4	8
Material lost as OAc^- (%)	16·5	26·9	30·8	34·4
Material lost as Cl^- (%)	51	14·5	9·9	5·3

The following preparative procedure was therefore adopted. The diol (4 mole), contained in a large Carius tube (about 700 ml. capacity), was cooled to −80°, and precooled acetyl chloride (4 mole) added. The tube was sealed and placed in an ice-bath, whereupon a vigorous reaction occurred. After being kept overnight, the tube was heated at 100° for 8 hr. Acids were then removed by treatment with potassium carbonate solution, and the product was distilled to give a colourless liquid, b. p. 50—100°/14 mm. This was acetylated at 100° with acetyl chloride (2 mole), and after acidic impurities had been removed the product was fractionated at reduced pressure to give a 65% yield of 1-acetoxy-3-chloropropane, b. p. 66·5—66·8°/14 mm. (Found : Cl, 25·9. Calc. for $C_5H_9O_2Cl$: Cl, 26·0%). Bennett and Heathcoat [10] record b. p. 66°/14 mm.

Oxa*cyclo*butane was prepared by the action of alkali on 1-acetoxy-3-chloropropane, according to Searles's procedure.[11] It was purified by refluxing it with, and distilling it from, freshly fused potassium hydroxide and fractionating the distillate, all these operations being carried out under nitrogen. The fraction, b. p. 48°/770 mm., n_D^{20} 1·3929 (Barrow and Searles [12] report b. p. 47°/750 mm., n_D^{25} 1·3893), was collected, dried *in vacuo* (BaO), and distilled in a good vacuum into the storage section of the polymerisation apparatus (Found : C, 62·1 ; H, 10·7. Calc. for C_3H_6O : C, 62·0 ; H, 10·4%).

(b) 2-*Methyloxa*cyclo*butane.* A mixture of acetoxychlorobutanes, $CH_3\cdot CHCl\cdot CH_2\cdot CH_2\cdot OAc$ and $CH_3\cdot CH(OAc)\cdot CH_2\cdot CH_2Cl$, b. p. 73·3—76·9°/15 mm. (Found : C, 48·0 ; H, 7·6 ; Cl, 24·3. Calc. for $C_6H_{11}O_2Cl$: C, 47·9 ; H, 7·4 ; Cl, 23·6%), was prepared from butane-1 : 3-diol in 70% yield, by the method described above for 1-acetoxy-3-chloropropane. 2-Methyloxa*cyclo*butane was prepared from the mixture of chlorobutyl acetates in 42% yield by the action of alkali, according to Searles's procedure for oxa*cyclo*butane.[11] This monomer, purified as described above, had b. p. 59·7—59·8°/760 mm., n_D^{20} 1·3919 (Found : C, 66·6 ; H, 11·3. Calc. for C_4H_8O : C, 66·6 ; H, 11·2%). Barrow and Searles [12] record b. p. 60°/747 mm., n_D^{25} 1·3890.

(c) 3 : 3-*Dimethyloxa*cyclo*butane.* 1-*Acetoxy*-3-*chloro*-2 : 2-*dimethylpropane,* b. p. 67·9—68·2°/10 mm., n_D^{20} 1·4325 (Found : C, 51·8 ; H, 8·3 ; Cl, 21·3. $C_7H_{13}O_2Cl$ requires C, 51·1 ; H, 8·0 ; Cl, 21·4%), was prepared in 83% yield from the corresponding diol by a slight modification of the method described above for 1-acetoxy-3-chloropropane. The initial reaction between 2 : 2-dimethylpropane-1 : 3-diol (prepared according to Whitmore *et al.*[13]) and acetyl chloride was carried out at 20°, and the Carius tubes were then heated to 140° for 48 hr. The acetylation and isolation procedures were as described above.

---

[9] Bogert and Slocum, *J. Amer. Chem. Soc.*, 1924, **46**, 763.

[10] Bennett and Heathcoat, *J.*, 1929, 271.

[11] Searles, *J. Amer. Chem. Soc.*, 1951, **73**, 124.

[12] Barrow and Searles, *ibid.*, 1953, **75**, 1175.

[13] Bernstein, Popkin, Whitmore, and Wilkins, *ibid.*, 1941, **63**, 126.

Application of Searles's procedure, for the preparation of oxa*cyclo*butane, to the action of alkali on 1-acetoxy-3-chloro-2 : 2-dimethylpropane gave very low yields of the cyclic ether, the principal product being *iso*butene (identified by its infrared absorption spectrum). Searles and Garlatowski [14] have reported that *iso*butene is the main product from the reaction of 3-bromo-2 : 2-dimethylpropanol with alkali. The following procedure was therefore adopted. Pentyl alcohol (400 ml.) was heated under reflux to 80°, and potassium hydroxide flakes (4 mole) added with constant stirring. When the alkali had dissolved, 1-acetoxy-3-chloro-2 : 2-dimethylpropane (1 mole) was added during 2 hr., the internal temperature being maintained between 100° and 110°. The liquid was distilled (stirring was continued to expedite the distillation), and the fraction of b. p. 70—135° collected. After being dried (K_2CO_3), this was fractionated to give two fractions : (1) b. p. 69—80° and (2) b. p. 80—83°; much pentyl alcohol remained in the pot. Fraction (1) was dried (K_2CO_3), refluxed with sodium, distilled, and added to fraction (2). The liquid so obtained was refluxed over sodium wire for several hours, then fractionated from the sodium (these operations being carried out under nitrogen) to give pure 3 : 3-dimethyloxa*cyclo*butane, b. p. 81·0°/765 mm., n_D^{20} 1·3980 (Found : C, 69·8; H, 11·9. Calc. for $C_5H_{10}O$: C, 69·7; H, 11·7%) in 40% yield. Barrow and Searles [12] record b. p. 76—78° for this compound, and Bennett and Philip [15] b. p. 78°/742 mm.

Solvents.—Ethyl chloride and methyl chloride, obtained from cylinders, were passed through sulphuric acid and stored *in vacuo* over calcium hydride.

Catalysts.—Boron trifluoride was prepared as described previously,[16] and the dihydrate according to Shirley.[17]

Polymerisation Techniques.—(a) *Polymerisations catalysed by boron trifluoride.* Measured quantities of monomer, solvent (when required), and catalyst were distilled *in vacuo* into a constricted glass tube cooled in liquid nitrogen. The tube was sealed, and warmed to the required temperature. Polymers of oxa*cyclo*butane were isolated by dissolving the contents of the tube in ether and, after ammonia had been passed in, cooling the solution to −80°, whereupon the polymer crystallised out and was filtered off. The frozen polymer was freed from solvent by placing it in a vacuum-desiccator, which was then evacuated continuously for 24 hr. Evaporation of the mother-liquor gave a crystalline material from which a tetramer was isolated (see below). Polymers of 2-methyloxa*cyclo*butane, and copolymers of this monomer with oxa*cyclo*butane, were isolated by dissolving the polymerisation product in ethanol and precipitating the polymer with distilled water. Volatile impurities were pumped off, leaving extremely viscous oils, which did not crystallise at room temperature or at −80°.

(b) *Polymerisations catalysed by boron trifluoride dihydrate.* Oxa*cyclo*butane (195 g.) and methyl chloride (490 ml.) were distilled, *in vacuo*, into a flask, fitted with a mechanical stirrer and a reflux condenser, which was cooled by liquid nitrogen. The mixture was warmed to −60°, and boron trifluoride dihydrate (22·1 ml.) added. Polymerisation commenced and the solvent refluxed vigorously. After 18 hr. the product was poured into ether (2 l.) and, when the methyl chloride had boiled off, the solution was treated, first, with aqueous sodium hydroxide, and then with water. After drying (K_2CO_3), polymer and tetramer were isolated as described above. The yield of polymer, m. p. 25°, $[\eta]$ *ca.* 0·05 dl. g.$^{-1}$, was 171 g., and the yield of tetramer 1 g.

The polymerisation of 3 : 3-dimethyloxa*cyclo*butane (175 g.) in ethyl chloride (490 ml.) solution, catalysed by boron trifluoride dihydrate (22·1 ml.), was carried out according to the procedure described in the previous paragraph. Evaporation of the ether solution gave a crystalline mass which was stirred and heated to 130° at 0·05 mm. for 24 hr., during which crystalline material distilled and condensed on the upper parts of the vessel. Thus were obtained 123 g. of polymer, m. p. 45°, $[\eta]$ *ca.* 0·05 dl. g.$^{-1}$, and 40 g. of crystalline material from which a tetramer was isolated (see below).

Viscosity Measurements.—The intrinsic viscosities of the polymers in benzene solution were measured at 20° with an Ostwald No. 1 viscometer.

Tetramers.—(a) 1 : 5 : 9 : 13-*Tetraoxa*cyclo*hexadecane.* Purification of the crude *tetramer* (obtained as described above) by sublimation at 0·6 mm. followed by recrystallisation from absolute ethanol at −80° gave white crystals, m. p. 70° [Found : C, 61·1; H, 10·6%; *M* (Rast), 230; *M* (Menzies–Wright), 223. $C_{12}H_{24}O_4$ requires C, 62·0; H, 10·4%; *M*, 232].

Tetramer (8 g.) and fuming hydrochloric acid (120 ml.) were heated in a sealed tube to 100°

---

[14] Searles and Garlatowski, *J, Amer. Chem. Soc.*, 1953, **75**, 3030.

[15] Bennett and Philip, *J.*, 1928, 1937.

[16] Barr and Rose, *J.*, 1953, 3766.

[17] Shirley, " Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, 1951, p. 35.

for 7 days with constant shaking. The organic material was extracted with pentane, dried (K_2CO_3), and fractionated to give 1 : 3-dichloropropane (8 g., 51%), b. p. 119°/748 mm., n_D^{20} 1·4484 (Found : Cl, 62·2. Calc. for $C_3H_6Cl_2$: Cl, 62·7%) : Smyth and McAlpine [18] record b. p. 120·2°/750 mm., n_D^{20} 1·4488.

(b) 3 : 3 : 7 : 7 : 11 : 11 : 15 : 15-*Octamethyl*-1 : 5 : 9 : 13-*tetraoxa*cyclo*hexadecane*. The material (90 g.) obtained from polymerisations of 3 : 3-dimethyloxa*cyclo*butane was sublimed at 130° in a good vacuum. Recrystallisation of the sublimed material from absolute ethanol gave the *tetramer* (33 g.), m. p. 157° [Found : C, 69·4; H, 11·5%; *M* (Menzies–Wright), 331. $C_{20}H_{40}O_4$ requires C, 69·7; H, 11·7%; *M*, 344]. Evaporation of the mother-liquors gave a sticky material (36 g.) which, after recrystallisation from acetone at −80°, had m. p. 44°. The infrared absorption spectrum of this material was identical with that of hydroxyl-terminated poly-3 : 3-dimethyloxa*cyclo*butane of low molecular weight.

The author thanks Messrs. D. A. Barr, J. Gray, and M. E. A. Cudby for experimental assistance, and Mr. R. G. J. Miller for measurement of the spectra.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, PLASTICS DIVISION,
WELWYN GARDEN CITY, HERTS.

[*Received, September 2nd*, 1955.]

---

[18] Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1935, **57**, 979.