[Contribution from the Division of Applied Chemistry, National Research Council]

Cationic Polymerization of Ethylene Oxide. II. Boron Trifluoride

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Received May 23, 1956

Polymerization of ethylene oxide by boron trifluoride differs from that by stannic chloride in a number of important respects. Reversible chain transfer occurs and the catalyst is not consumed, yet in spite of the continued catalyst activity chain growth ceases at a relatively low molecular weight and is replaced by dimer formation. Since dimer formation seems to result from a depolymerization reaction of the active chain, the limiting molecular weight must be due to an equality of the rates of polymerization and depolymerization at this point. This equality of rates is not the result of a true equilibrium so presumably results from a molecular weight dependence of one or both of the rates.

The previous paper described the polymerization of ethylene oxide by stannic chloride and discussed a possible mechanism for the process. Catalysis by boron trifluoride, although generally similar to that by stannic chloride, shows several remarkable differences arising partially, but not entirely, from the absence of chain termination and catalyst destruction. Perhaps the most interesting difference observed between the two catalysts lies in the molecular weight of the polymer produced, for whereas that from stannic chloride continues to grow until terminated, that from boron fluoride reaches an "equilibrium" molecular weight. This molecular weight can be approached either from monomer or from higher molecular weight polymer but seems almost independent of all reaction variables. This paper reports therefore not only the results of polymerization studies but also some work on the depolymerization of polyglycols by boron trifluoride.

Experimental

The apparatus and techniques in this study were very similar to those used in the reaction with stannic chloride. It was found necessary, however, to condense all the reactants together with liquid nitrogen and to start the reaction by warming to reaction temperature because, due to the appreciable vapor pressure of boron trifluoride, some vapor phase reaction occurred if monomer was distilled into the reaction vessel.

Boron trifluoride was purified by passing through a series of traps held at −80°, and stored at liquid nitrogen temperature.

The polyethylene glycols added to reaction mixtures were commercial samples which had been dried in a vacuum oven.

Results

The products of the reaction in solution near room temperature were determined by allowing a 2 *M* solution of ethylene oxide to react with 0.02 *M* boron trifluoride in ethyl chloride. After separation by distillation, the volatile portion of the products was examined in the mass spectrometer and found to have a spectrum consistent with dioxane containing 12% 2-methyl-1,3-dioxolane. Both the ultraviolet and the infrared spectrum of the mixture suggested the presence of a little of a carbonyl compound, but it was not identified. The nonvolatile residue from this reaction was discolored. If, as described later, a trace of water was present in the reaction mixture, the polymeric material was a colorless low melting wax, and had the infrared spectrum of a polyethylene glycol.

In anhydrous ethylene chloride, ethylene oxide reacted with boron fluoride to form a sticky, dark-colored precipitate which slowly went into solution as more oxide disappeared. When the reaction mixture had become homogeneous, monomer reacted smoothly and continued to do so after further additions of oxide, at a rate which appeared to be first order in catalyst but only slightly above zero order in monomer. The slow initial rate, together with the discoloration of the reaction mixture suggested, however, that some decomposition was necessary to initiate polymerization, a view confirmed by the observation that addition of water to the reaction mixture in concentration equal to that of the catalyst eliminated precipitation, discoloration and induction period. Under these latter conditions initial rates readily could be followed so all further experiments were conducted with boron fluoride–water mixtures as catalyst. The results of these experiments are shown in Table I.

Table I

Reaction Rates of Boron Trifluoride with Ethylene Oxide in the Presence of Water

(C_2H_4O), moles/l.	(BF_3), mole/l.	(H_2O), mole/l.	Initial rates, mole/l./min.	k, l.$^{1/2}$ m.$^{-1/2}$ min.$^{-1}$
2.0	0.01	0.01	0.0147	
2.0	.02	.02	.0295	0.92
2.0	.03	.03	.0408	.96
2.0	.04	.04	.0555	.95
2.0	.05	.05	.0667	.99
1.0	.01	.012	.0104	.97
1.0	.01	.012	.0101	.94
1.0	.02	.024	.0193	.90
1.0	.03	.036	.0252	.92
1.0	.04	.048	.0370	.99
2.0	.02	.024	.0302	.91
0.63	.02	.024	.0142	.89
0.39	.02	.024	.0107	.85
			Mean	0.93

The effect of variation of catalyst concentration in the presence of equimolar concentrations of water is shown in Fig. 1, and the order appears to be first. The dependence on monomer concentration is shown in Fig. 2, the order being 0.67. Hence the initial rates are governed by the expression

$$-\, d(C_2H_4O)/dt = k'(BF_3)(C_2H_4O)^{0.67}$$

when the concentrations of water and of boron trifluoride are equal.

Since successive additions of monomer gave almost identical rates, the catalyst apparently is not consumed during the reaction and therefore the above expression should express the entire reaction curve, rather than just the initial part of it. In fact, rate constants which adequately account for

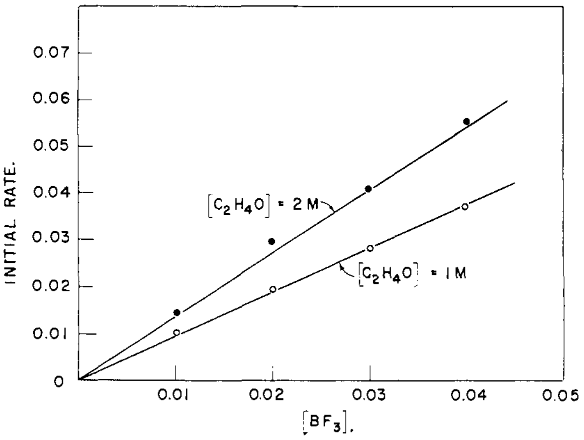


Fig. 1.

over 90% of the total reaction can be obtained from the more easily integrated expression

$$-\,d(C_2H_4O)/dt = k(BF_3)(C_2H_4O)^{1/2}$$

and are presented as k in Table I. It is interesting that this constant is about half that obtained from a similar rate expression for stannic chloride catalysis since each stannic chloride molecule appears to initiate two chains.

The Arrhenius activation energy from initial rates at three temperatures was found to be 14.7 kcal., in close agreement with that observed for stannic chloride.

Water, provided that its concentration is at least equal to that of the boron fluoride, does not greatly affect the reaction rate, but does affect the proportion of polymer found in the product. From the data in Table II, it is clear that a polymer molecule is formed for each molecule of water present initially and that this polymer molecule grows in all cases to a molecular weight of about 700. The curves in Fig. 3 show that polymer growth occurs almost entirely in the initial stages of the reaction and is replaced by dioxane formation once the maximum molecular weight has been reached. Other hydroxylic compounds can replace water as the co-catalyst. Ethyl alcohol yields dioxane and polymer of molecular weight 600–700, while polyethylene glycol of molecular weight 400 when added to the reaction mixture in place of water gives a final product of weight 600. The temperature dependence of the final molecular weight is shown in Table III.

TABLE II

EFFECT OF REACTANT CONCENTRATION ON POLYMER FORMATION

BF_3, mole/l.	C_2H_4O moles/l.	H_2O, mole/l.	Wt. polymer/l. grams	Mol. wt.	Polymer, mole/l.
0.02	2.0	0.100	60.5	730	0.083
.02	2.0	.080	57.1		
.02	2.0	.074	54.9	760	0.072
.02	2.0	.050	36.0	770	.047
.02	2.0	.039	32.2		
.02	2.0	.026	21.8		
.02	2.0	.020	20.0	770	.026
.03	2.0	.030	22.4	730	.031
.04	2.0	.040	30.6	760	.041
.05	2.0	.050	32.0	670	.048
.02	1.0	.050	27.6	560	.049
.02	1.0	.100	35.3		
.02	0.5	.050	13.1		
.02	0.5	.100	21.0		

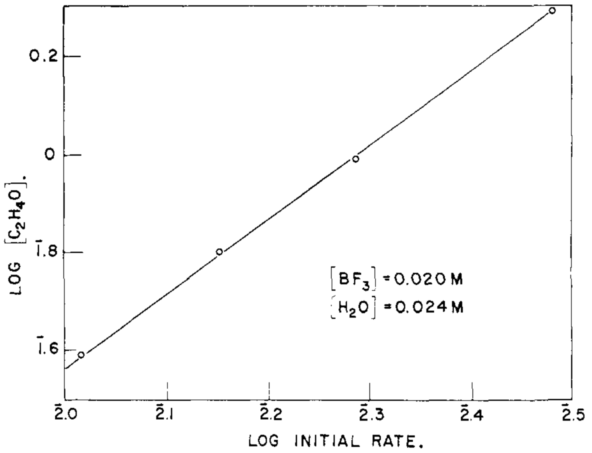


Fig. 2.

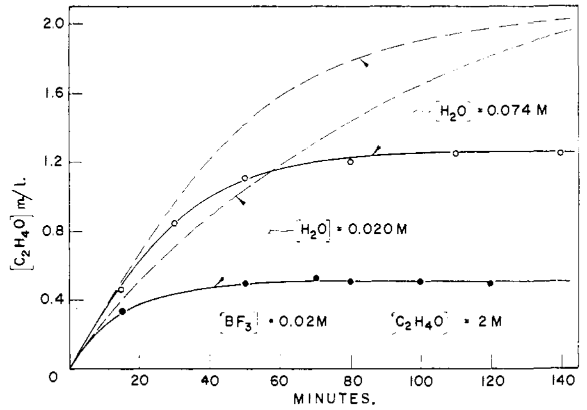


Fig. 3.—Dotted lines, total ethylene oxide reacted; solid lines, oxide reacted to form polymer.

High molecular weight polyethylene glycols are depolymerized by ethylene oxide and BF_3. A polymer of weight 4000 dissolved in ethylene chloride remained unchanged after 16 hours in the presence of boron trifluoride, but if oxide were present as well, the amount of polymer decreased, monomer was consumed and dimer was formed. If sufficient ethylene oxide was present initially the molecular weight of the polymer decreased to 600 while lesser amounts of oxide resulted in intermediate weights as shown in Table IV. Polymer of molecular weight 20,000 behaved similarly. Water added to the reaction mixture caused some increase in the number of chains but did not otherwise affect the depolymerization.

TABLE III

VARIATION OF MOLECULAR WEIGHT WITH TEMPERATURE

Temp., °C.	30	20	0	−20
Mol. wt.	550	760	880	925

To determine whether depolymerization is initiated at the terminal hydroxyl group, polymer of

TABLE IV

DEPOLYMERIZATION OF POLYETHYLENE GLYCOL OF MOL. WT. 4000 IN ETHYLENE CHLORIDE

Initial polymer concentration 1.75 g./20 cc.; BF_3, 0.02 *M*

Init. (C_2H_4O), moles/l.	Loss in wt. polymer, g.	Mol. wt. final
0.49	0.699	1650
.73	.790	1230
.99	.921	1070
1.50	1.011	650
2.00	1.070	640

weight 4000 was fully methylated, then reacted as before. It was found that the rate of oxide disappearance was reduced, the final molecular weight was only about 400, and the reaction mixture discolored in much the same way as did the anhydrous mixture of ethylene oxide and boron trifluoride. It would seem therefore that attack is preferentially at the hydroxyl group but can occur elsewhere along the chain As a result the number of polymer molecules increases somewhat in all depolymerizations, in some cases to nearly twice the initial concentrations.

To obtain more insight into the depolymerization, a polymer of weight 4000 was treated with fully deuterated ethylene oxide in methylene chloride solution. The volatile products were separated by distillation under vacuum, followed by fractionation, and examined in the mass spectrometer with the results shown in Table V. The infrared spectrum of the polymeric residue showed the presence of both C–H and C–D bonds in roughly comparable amounts.

TABLE V

PRODUCTS OF DEPOLYMERIZING POLYETHYLENE GLYCOL WITH C_2D_4O

$C_4H_8O_2$	59%
$C_4H_4D_4O_2$	14%
$C_4D_8O_2$	26%

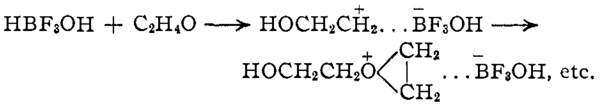
All 2-Me-1,3 dioxolane fully deuterated.

Discussion

It is conceivable, in view of the part played by water in this reaction, that the polymerization proceeds through a simple stepwise, acid-catalyzed addition of oxide to the hydroxyl group of the growing chain, *i.e.*

$$ROH \xrightarrow[\text{oxide}]{HBF_3OH} ROCH_2CH_2OH \longrightarrow R(OCH_2CH_2)_2OH \longrightarrow \text{etc.}$$

This mechanism, however, is difficult to reconcile with the observed kinetics and cannot apply to the kinetically similar stannic chloride system. A mechanism analogous to that postulated in the previous paper therefore seems preferable and can easily be formulated if one supposes that the conjugate acid HBF_3OH reacts with ethylene oxide to form the required oxonium ion, *viz.*



$$HBF_3OH + C_2H_4O \longrightarrow HOCH_2\overset{+}{C}H_2\ldots\overset{-}{B}F_3OH \longrightarrow HOCH_2CH_2\overset{+}{O}\Big\langle\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\ldots\overset{-}{B}F_3OH, \text{ etc.}$$

Chain transfer may occur in a variety of ways which lead to a correspondence between the number of polymer molecules and the water added initially, but it is necessary to suppose that the transfer reaction is reversible to account for the continued growth of low molecular weight polymer and for the retarded rate of depolymerization of high molecular weight polymer resulting from the methylation of the terminal hydroxyl groups.

The most interesting feature of the boron trifluoride reaction is the existence of a constant final molecular weight which can be approached from either higher or lower weights and which appears to be almost independent of all reaction variables. At first sight such a condition would appear to result from the establishment of an equilibrium but in fact no strict concentration equilibrium appears possible. It seems to follow therefore that the "equilibrium" molecular weight must result from a balance between the rates of polymerization and depolymerization at this point but this is only possible if, in contradiction to current theory, one or both of these rates varies with the molecular weight of the polymer.

Depolymerization requires the presence not only of BF_3 but also of oxide. From the quantities of undeuterated and partially deuterated dioxane produced from fully deuterated oxide and normal polymer it seems clear that when reaction of a molecule of oxide activates the chain, several molecules of dioxane are split off (about seven oxide residues for each oxide added, in the experiment shown in Table V). The process continues, perhaps in stepwise fashion, until the molecular weight is reduced to about 700. Fully deuterated dioxane is then formed by reaction at the active end of the equilibrium polymer. (Dioxolane appears to be a by-product formed directly from oxide since it is all fully deuterated.)

Obviously, in order to obtain an equilibrium molecular weight, one oxide residue must be removed from the chain as dioxane for each oxide molecule reacting. In the experiment with deuterated oxide, however, the ratio of residues eliminated to oxide reacted appears to be about 7:1. It seems therefore that the ratio increases with the molecular weight of the polymer and that the 7:1 figure is the average value of the ratio as the molecular weight is decreased from 4000 to 700.

It is difficult in view of the foregoing results to account for the fact that stannic chloride easily produces polymers of molecular weight 3000 or higher; in fact, in pure oxide, polymers of weight 10,000 have been obtained. It may be that the increased rigidity of the active system, due to the fact that both ends of two chains are associated with the catalyst, prevents the ionic charge from moving rapidly down the chain in depolymerization. Also of interest is the failure of aluminum chloride to produce polymer; results suggest that this is due to a high rate of termination rather than to a high rate of depolymerization because no dioxane is formed.

Acknowledgment.—The authors make grateful acknowledgment of the assistance they received from Dr. A. W. Tickner in the mass spectrometric investigation of products and from Dr. L. C. Leitch in the preparation of deuterated ethylene oxide.

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