acid, m.p. and mixture m.p. 150–151°, 21% yield. A similar oxidation of cyclohexanone oxime gave adipic acid in 12% yield.

Trace amounts of diphenylfuroxane were obtained from the oxidation of benzil dioxime with dinitrogen tetroxide.

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Cationic Polymerization of Ethylene Oxide. I. Stannic Chloride

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The polymerization of ethylene oxide by stannic chloride in ethylene chloride solution at ordinary temperatures produces polymer of molecular weight below 5000, dioxane and small amounts of dioxolane. Two polymer molecules are formed for each molecule of stannic chloride; dioxane formation is an alternative reaction at the active end of the growing chain. The rate of disappearance of oxide is controlled by the propagation step and is given by the expression $k(\text{oxide})^{0.45}(\text{SnCl}_4)^{1.2}$ obtained from initial rates. Chain termination occurs with catalyst destruction and without transfer at a rate which appears to be first order in catalyst. A mechanism by which propagation occurs through an intermediate oxonium ion is proposed to account for the results.

The polymerization of ethylene oxide may be effected with either acidic or basic catalysts to give linear polyethers with a considerable range of molecular weights. The base-catalyzed reaction has been studied comprehensively by Perry and Hibbert[1] and is of the polycondensation type, but with the exception of a study by Meerwein, *et al.*,[2] of trialkyl oxonium ions and their reactions with epichlorohydrin, and some remarks by Emeleus and Stone[3] on the reaction of boron trifluoride with ethylene oxide, little work has been reported on the acid-catalyzed polymerization. This paper describes the results of some studies on the polymerization of ethylene oxide by stannic chloride, and is followed by one describing the polymerization by boron fluoride. Of the Friedel–Crafts catalysts tested, only these two gave polymeric products; aluminum, titanium and germanium chlorides are ineffective.

Experimental

Materials.—Ethylene oxide was purified by low temperature distillation, by distillation at −78° from dried sodium hydroxide pellets and finally by drying over barium oxide, all under vacuum.

Stannic chloride was fractionally distilled from tin metal, then twice distilled under vacuum.

Solvents were fractionated from phosphorus pentoxide. Ethylene chloride was treated with aluminum chloride, washed and dried before fractionating.

Method.—Polymerizations were carried out in an all-glass vacuum system and the rate of reaction in ethylene chloride solution followed by the decrease in vapor pressure of the reaction mixture. The relationship between oxide concentration and vapor pressure was linear and hence readily determined from known mixtures.

Stannic chloride and water were measured out by allowing the liquid, at controlled temperature, to evaporate into bulbs of known volume until equilibrium was established. The quantity was then determined from the vapor pressure of the liquid.

Ethylene oxide and ethyl chloride were measured in the gas phase, but the less volatile solvents were pipetted into a trap containing phosphorus pentoxide and degassed before distilling into the reaction vessel.

Catalyst, water if any, and solvent in that order were condensed into the reaction vessel and brought to reaction temperature. Ethylene oxide was then rapidly distilled in from a small side arm on the main reaction vessel. Magnetic stirring established equilibrium within three minutes.

Ethyl chloride was employed as solvent when reaction products were to be determined because it could be separated readily by distillation. Ethylene chloride was used for most of the kinetic studies because of its lower vapor pressure.

Reaction products were isolated by treating a 10% solution of ethylene oxide with one mole per cent. stannic chloride at 20°. Solvent, excess oxide and volatile products were removed by distillation, leaving a white wax having an infrared spectrum identical with that of a polyethylene glycol of similar melting point. The volatile product was found, by mass spectrometer analysis, to consist of 92% dioxane and 8% 2-methyl-1,3-dioxolane.

Molecular Weights.—Molecular weights were determined viscometrically in ethylene chloride, using Ostwald viscometers with flow times of about two hundred seconds at 20°. For molecular weights less than 1000 the relationship

$$\eta_{sp}/c = 0.048 + 0.000204\ M$$

was used where c is in base moles per liter. This expression was obtained using commercial polyglycols whose molecular weights were determined by end-group analysis and by the depression of the benzene freezing point.

Molecular weights above 1000 were given by the expression

$$\eta_{sp}/c = 0.160 + 0.000089\ M$$

which was obtained from commercial polyglycols whose molecular weights were first determined in carbon tetrachloride using the viscometric data of Fordyce and Hibbert.[4]

Polymer samples were obtained from the reaction mixture by quenching aliquots in aqueous alcohol, evaporating on a steam-bath, then drying for two or three hours under vacuum at 70°.

Results

When molar solutions of ethylene oxide were treated in ethylene chloride with a monomer–catalyst ratio of 100:1, reaction stopped before all oxide was consumed. Addition of monomer did not regenerate the reaction but a higher initial concentration of catalyst caused it to go to completion. Apparently stannic chloride is consumed in the reaction; the alternative possibility that the catalyst itself contained some unidentified co-catalyst which was consumed seems unlikely. Because of the consumption of stannic chloride it was necessary to use initial rates to obtain the reaction order. The results are shown in Figs. 1–2 and lead to the kinetic equation

$$-\mathrm{d}(\mathrm{C_2H_4O})/\mathrm{d}t = k(\mathrm{C_2H_4O})^{0.45}(\mathrm{SnCl_4})^{1.2} \qquad (1)$$

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[1] S. Perry and H. Hibbert, THIS JOURNAL, **62**, 2599 (1940).

[2] H. Meerwein, U. Eisenmenger and H. Matthiae, *Ann.*, **560**, 150 (1950).

[3] F. G. A. Stone and H. J. Emeleus, *J. Chem. Soc.*, 2755 (1950).

[4] R. Fordyce and H. Hibbert, THIS JOURNAL, **61**, 1912 (1939).

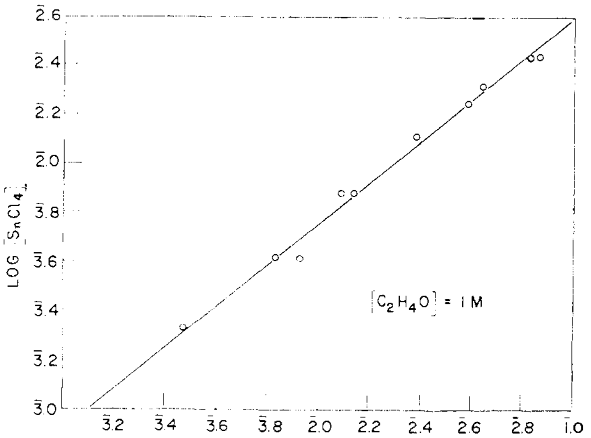


Fig. 1.

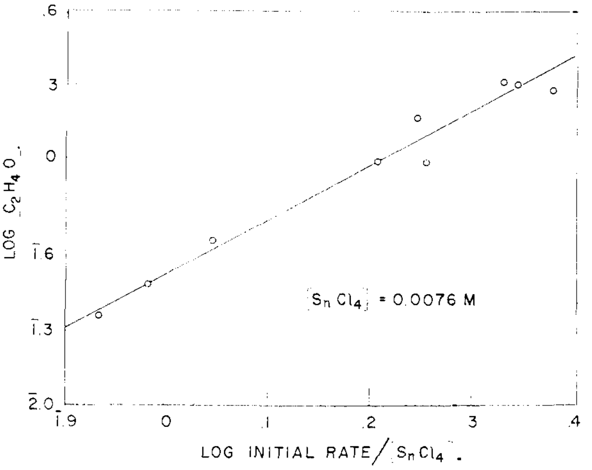


Fig. 2.

The ratio of polymer to dioxane–dioxolane was determined at various stages of the reaction by removing aliquots and determining polymer. The difference between the amount of oxide consumed and that recovered as polymer was assumed to be the dimers. The results are shown in Table I.

Table I

Formation of the Polymer over the Course of the Reaction

(C_2H_4O), 2 *M*; ($SnCl_4$), 0.0072 *M*; temp. 20°

Time, min.	C_2H_4O consumed, moles/l.	Polymer formed, base moles/l.	Mol. wt.	Moles (polymer) / Moles (catalyst)
13	0.20	0.2	*ca.* 600	2.0
29.5	.40	.35	1010	2.1
51	.60	.51	1530	2.0
81	.80	.60	2090	1.7
120	1.00	.73	2560	1.7
190	1.20	.81	3000	1.6
315	1.42	.91	3630	1.5
—	1.67	1.01	3830	1.6

The activation energy, from initial rates at three temperatures over a 30° range, was found to be 15 kcal., exceptionally high for a cationic polymerization but consistent with a slow propagation step involving the opening of an oxirane ring.

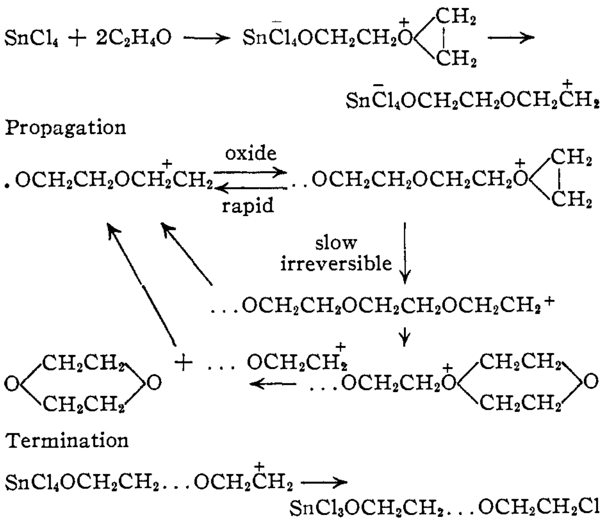
From the foregoing data it may be concluded that each stannic chloride molecule rapidly initiates two polymer chains which slowly increase in length during the course of the reaction, and undergo termination with no transfer and with destruction of the catalyst. The decrease in the polymer–catalyst mole ratio may be attributed to the divergence of the number average and weight average molecular weights as the molecular weight distribution becomes wider. This broadening of the distribution obviously must occur if the number of active chains decreases steadily during the polymerization as the result of a slow termination reaction.

The fact that the number of polymer molecules remains constant throughout the polymerization means that the catalyst is either consumed in initiating the chain, or remains associated with it until destroyed in the termination. It follows that the formation of dioxane must occur along with chain propagation at the active end of the chain and it is therefore not surprising that the ratio of dioxane to propagation remains fairly constant, throughout much of the reaction.

Traces of water may perhaps be necessary as cocatalyst in the reaction mixture, but drying of apparatus and materials was not sufficiently rigorous to establish this point. Addition of water in concentration equal to that of the catalyst completely poisoned the reaction. The solvent apparently takes no direct part in the reaction which proceeds with equal facility, though not entirely homogeneously, in *n*-heptane.

Discussion

It is difficult to formulate a reaction scheme which accounts for all of the experimental data but the following series of reactions seems to explain most of them.



$$SnCl_4 + 2C_2H_4O \longrightarrow Sn\bar{C}l_4OCH_2CH_2\overset{+}{O}\langle(CH_2)_2 \longrightarrow Sn\bar{C}l_4OCH_2CH_2OCH_2\overset{+}{C}H_2$$

$$SnCl_4OCH_2CH_2 \ldots OCH_2\overset{+}{C}H_2 \longrightarrow SnCl_3OCH_2CH_2 \ldots OCH_2CH_2Cl$$

Formation of the oxonium ion in the initiation step is highly probable in view of the work of Meerwein, *et al.*[5] Since two molecules of polymer are formed for each molecule of catalyst, and since

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[5] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

the coördination number of tin is six, it must be supposed that two chains are initiated by, and remain attached to, each catalyst molecule.

The termination reaction is likewise highly probable. Reactions of the type

$$\mathrm{MCl}_n + n\mathrm{C_2H_4O} \longrightarrow \mathrm{M(OCH_2CH_2Cl)}_n$$

are common between ethylene oxide and metal chlorides and appear to account for the fact that aluminum chloride is not catalytic in the present reaction. It was found, moreover, that only half of the chlorine present in the reaction mixtures could be recovered at the end of polymerization with cold silver nitrate. No real evidence could be found for chlorine in the polymer or volatile products, but this could be due to the small amount present.

Such a termination mechanism would be independent of monomer and first order in catalyst concentration. If the equations

$$-\mathrm{d(C_2H_4O)}/\mathrm{d}t = k_1(\mathrm{C_2H_4O})^{1/2}(\mathrm{SnCl_4}) \qquad (2)$$

$$-\mathrm{d(SnCl_4)}/\mathrm{d}t = k_2(\mathrm{SnCl_4})^n \qquad (3)$$

are integrated and combined, one obtains the expression

$$M^{1/2} - (M - x)^{1/2} = \frac{k_1c}{2k_2}(1 - e^{-k_2t}) \qquad (4)$$

when $n = 1$ and where M and c are the initial concentrations of monomer and catalyst, respectively. It follows that for any given time, t, in a series of runs, $M^{1/2} - (M - x)^{1/2}/c$ should be constant and this in fact seems to be true as is seen in Table II where values of this quantity are given for t = 30 min. Similar results were found for values to t from 10 to 60 min., but no such constancy was found for other integral values of n.

TABLE II

RATE CONSTANTS DERIVED FROM EQUATIONS 2 AND 3, ASSUMING A VALUE OF k_2 OF 0.019

Initial concn. $\mathrm{C_2H_4O}$	Initial concn. $\mathrm{SnCl_4}$	$\frac{M^{1/2} - (M-x)^{1/2}}{C}$	k_1 (l.$^{1/2}$ m.$^{-1/2}$ min.$^{-1}$) calcd.	k_1 from init. rates
1.022	0.00215	18.6	1.57	1.39
1.018	.00410	18.5	1.83	2.07
1.059	.00415	19.0	1.69	1.64
0.978	.0076	20.6	1.72	1.82
.990	.0076	20.4	1.77	1.62
.982	.0130	18.1	1.66	1.85
.983	.0174	21.2	1.91	2.23
1.000	.0204	19.8	1.79	2.15
1.000	.0269	18.4	1.89	2.51
1.035	.0270	17.7	1.79	2.72
2.010	.0072	20.7	1.83	1.55
1.910	.0072	22.6	2.05	1.73
1.480	.0074	20.3	1.81	1.45
0.468	.0077	18.9	1.73	1.72
.310	.0078	20.4	1.87	1.73
.230	.0078	21.2	1.78	1.79
		Mean	1.79	1.88

The termination constant, k_2, can be evaluated by substituting the experimental data into equation 4 and its average value within runs and between runs was found to be 0.019 min.$^{-1}$. The equation was then solved for k_1 and these calculated values, which hold for about two catalyst half-lives, are compared in Table II, with the values of k_1 obtained from initial rates and equation 2. The agreement is reasonably good except at high catalyst concentrations where the discrepancy may be the result of an error in the initial rate due to the amount of oxide reacting directly with catalyst.

The propagation reaction presents the greatest problem in interpreting the data. It seems highly improbable that it proceeds through a direct carbonium ion mechanism such as that suggested for the isobutylene polymerization,[6] because the ion would have too short a lifetime to account for the slow rate of chain growth and would not account for the apparent half-order dependence on monomer concentration. In the scheme as shown, the propagation may be represented as

$$\text{oxide} + P_i \underset{}{\overset{K}{\rightleftarrows}} P_i\cdot\text{oxide} \xrightarrow{k_p} P_{i+1}$$

and leads to the rate expression, where $P = P_i\cdot$oxide $+ P_i$

$$-\frac{\mathrm{d(oxide)}}{\mathrm{d}t} = \frac{k_pKP(\mathrm{C_2H_4O})}{1 + K(\mathrm{C_2H_4O})} \qquad (5)$$

which for initial rates, where $P = 2(\mathrm{SnCl_4})$, will approximate to the expression

$$-\frac{\mathrm{d(oxide)}}{\mathrm{d}t} = K'(\mathrm{SnCl_4})(\mathrm{C_2H_4O})^n$$

where $0 < n < 1$. The observed order of monomer disappearance would therefore be fractional but not necessarily one-half. Equation 5 is not unlike that proposed by Fontana and Kidder[7] to describe the polymerization of propylene by aluminum bromide–hydrogen bromide, a reaction which shows some similarity to the present case.

Equation 5 can be solved for K and k_p by plotting $1/M$ against $\mathrm{SnCl_4}$/initial rate. A reasonably good straight line is obtained and from the slope and intercept of this line, k_p and K are found to have the values 1.3 min.$^{-1}$ and 1.8, respectively.

The formation of dioxane can be explained by supposing that the carbonium ion attacks its own chain as shown. Since the expression for initial rates seems to hold even after considerable dioxane formation, and since addition of dioxane to the reaction mixture has little inhibiting effect on the rate of oxide disappearance, it must be supposed that oxide rapidly displaces dioxane from the chain end.

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[6] A. G. Evans and J. Polanyi, *J. Chem. Soc.*, 252 (1947).

[7] C. M. Fontana and G. A. Kidder, THIS JOURNAL, **70**, 3745 (1948).