

*The Kinetics and Mechanism of the Polymerization of Ethyleneimine.*

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The polymerization of ethyleneimine catalyzed by water and by various organic acids has been investigated by dilatometric kinetic measurements and by paper-chromatographic examination of the products. Pure, dry ethyleneimine reacts very slowly, even at high temperatures; traces of water greatly increase the rate. Acid catalysts produce much greater rates even at lower temperatures; water is not essential as a co-catalyst for these. The results are interpreted in terms of a stepwise reaction of iminium ions with uncharged imine-rings. Though the reaction is an addition polymerization, and there are, at any instant, only a small number of reactive iminium ions present, the overall characteristics are similar to those of a typical stepwise poly-condensation because of a very rapid "transfer equilibrium" of hydrogen ions between the various entities present.

The kinetics of reaction for various acids have been examined. The fractional consumption of catalyst during the reaction is as great as, or greater than, the fractional consumption of monomer; the kinetics of monomer conversion are therefore largely determined by the kinetics of catalyst destruction and hence vary from one catalyst to another. With weak acids it is assumed that ion-pairs, rather than free iminium ions and anions, are present.

Of the many polymerizations known only two, vinyl polymerization and polycondensation, have until recently been extensively investigated physicochemically to elucidate details of the reaction mechanism. Recently a third type, the formation of polypeptides from *N*-carboxy-anhydrides, has begun to be similarly investigated. Amongst polymerizations of which little is known regarding exact details of mechanism (though much empirical information may be available) is the addition polymerization of the three-membered ring compound, ethyleneimine. The earlier investigations of Kern and Brenneisen (*J. prakt. Chem.*, 1941, 159, 193, 219) and of Jones and his co-workers (Jones, Langsjoen, Neumann, and Zomlefer, *J. Org. Chem.*, 1944, 9, 125; Jones, *ibid.*, p. 484) had established certain facts bearing on the mechanism, and these are summarized below.

Amongst the findings of Kern and Brenneisen are the following : (i) Acids catalyze the polymerization. In particular, 40% aqueous hydrogen bromide and borofluoroacetic, toluene-*p*-sulphonic, and sulphanilic acid were employed. (ii) Various bases known to catalyze the polymerization of ethylene oxide proved ineffective for the polymerization of ethyleneimine. (iii) Peroxides, used under similar conditions to those employed for the acid catalysts, did not cause polymerization, but since the conditions involved temperatures of 40° or 50°, at which the peroxides would not decompose appreciably, these experiments are inconclusive. (iv) Inhibitors of free-radical vinyl polymerizations do not inhibit ethyleneimine polymerization. (v) The reaction frequently proceeds explosively, particularly if a certain catalyst concentration or a certain temperature is exceeded. (vi) The reaction catalyzed by sulphanilic acid seems to be intermediate between a first- and a second-order reaction in ethyleneimine. (vii) Acetylation of the polymer yielded a 1 : 1 acetyl derivative, but benzoylation gave derivatives apparently containing more nitrogen than corresponded to a 1 : 1 compound.

Jones and his co-workers found, amongst other results, that : (i) Ethyleneimine in the absence of catalysts is very stable, even at 150°. (ii) Substances which catalyze polymerization are those capable of producing quaternary iminium nitrogen, *i.e.*, acids, alkylating agents, etc. (iii) The (refractometrically measured) kinetics of polymerization of ethyleneimine in dilute hydrochloric acid are complicated. The reaction is of a very high order in ethyleneimine, though the quarter-life is inversely proportional to the initial ethyleneimine

concentration; the half-life was inversely proportional to the initial acid concentration. Benzoylation of poly(ethyleneimine) gave a substance whose nitrogen content corresponded approximately to that of a 1 : 1 compound.

It seems therefore that the reaction proceeds *via* iminium intermediates [e.g. (I)], but the course of the reaction is not clear and there is uncertainty as to whether the polymer is linear or branched.

#### EXPERIMENTAL

**Materials.**—The procedures used for preparing ethyleneimines followed these workers: Ethyleneimine, Wenker (*J. Amer. Chem. Soc.*, 1935, **57**, 2328). *N*-(*n*-Butyl)ethyleneimine, Elderfield and Hageman (*J. Org. Chem.*, 1949, **14**, 605). *N*-(2-Aminoethyl)ethyleneimine ("ethyleneimine dimer") from 2-amino-2'-hydroxydiethylamine (Jones *et al.*, *loc. cit.*).

*n*-Butylamine and piperidine were fractionally distilled before use. The acid catalysts used were recrystallized commercial samples. "AnalaR" phenol was used without further purification.

**Density and Thermal Expansion of Ethyleneimine and Volume Change on mixing with Water.**—These quantities were required for the analysis of dilatometric kinetic measurements. Density was measured by distilling sodium-dried ethyleneimine *in vacuo* into dilatometers (1-mm. bore "Veridia" stems; bulb capacity approx. 0.5 ml.) calibrated with absolute alcohol.  $d_4^{25}$  was  $0.831 \pm 0.001$ , and over the range 25—65° the volume coefficient of expansion was  $1.3 \times 10^{-3}$  (volume per unit volume at 25° c per °c). By extrapolation  $d_4^{100}$  should be 0.756 (Found, by immersing a dilatometer in a steam-bath, 0.752) (Gabriel and Stelzner, *Ber.*, 1895, **28**, 2929, give the s. g. at 24° as 0.8321, corresponding to  $d_4^{25}$  0.831, and Jones *et al.*, *loc. cit.*, give  $d_4^{25}$  0.835, corresponding to  $d_4^{25}$  0.832, both in agreement with the present value).

The volume contraction on mixing ethyleneimine and water was measured in a small pycnometric flask and in dilatometers. Five measurements for mixtures ranging from 10% to 70% (by wt.) of water gave a value of  $23 \pm 4\%$  for the change in volume per volume of water used in forming a 1 : 1 hydrate (*i.e.*, where the molar concentration of water was greater than that of ethyleneimine, the volume change was calculated as a percentage of the volume of water equivalent to the ethyleneimine used). This volume change is much less than those for water plus methylamine or ethylamine, which (calculated from data in Beilstein's "Handbuch") are of the order of 40—60%. Similar experiments on mixtures of ethyleneimine and ethanamine showed that any volume change occurring was within the limits of experimental error.

**$pK_b$  of Ethyleneimine and of *N*-(*n*-Butyl)ethyleneimine.**—Certain features of the polymerization suggested that ethyleneimine was an abnormally weak base compared with aliphatic amines. This was tested by pH titration of approximately 0.01*N*-ethyleneimine solution with 2*N*-hydrochloric acid at 25°, with the arrangement described by Waley and Watson (*Biochem. J.*, 1953, **55**, 328). The total titre was within 1% of the theoretical value, and the titration curve was perfectly reproducible.

The basic dissociation constant  $K_b$  is defined as  $K_b = (\text{BH}^+)(\text{OH}^-)/(\text{B})$ , the terms in parentheses representing activities; if the Debye-Hückel relation for activity coefficients is applied, then

$$pK_b = pK_w - \text{pH} - \log[\text{BH}^+]/[\text{B}] + 0.5\sqrt{\mu} - C'\mu,$$

where  $C'$  is a constant and  $\mu$  the ionic strength (cf. Glasstone, "The Electrochemistry of Solutions," Methuen, London, 1937, Chap. IX). From the complete titration curve,  $pK_b$  was calculated at values of  $[\text{BH}^+]/[\text{B}]$  from 0.1 to 5, neglecting  $C'\mu$ ;  $pK_b$  so obtained ranged from 6.045 to 6.155, corresponding to  $K_b = 7 \times 10^{-7}$  to  $9 \times 10^{-7}$ .  $K_b$  for ethyleneimine is thus some 100 times less than for most aliphatic amines. Similar measurements on *N*-(*n*-butyl)ethyleneimine gave  $K_b = 6.5 \times 10^{-7}$  to  $8 \times 10^{-7}$ .

It seems likely that the abnormally low basicity of ethyleneimine and the instability of the three-membered ring under the influence of acids are related phenomena. The abnormal value to which the C-N-C bond-angle in ethyleneimine is constrained presumably affects the electronic structure and hence the availability of the nitrogen lone-pair electrons for dative-bond formation; correspondingly, if such a bond is formed by addition of a proton, the stability of the ring is impaired.

**Estimation of Percentage Conversion of the Reaction Mixture.**—Kern and Brenneisen (*loc. cit.*) estimated the residual ethyleneimine by chilling to stop the reaction and distilling the ethyleneimine *in vacuo* into standard acid; the back-titration of the excess of acid and a direct weighing

of the polymer residue gave concordant results, but in the writer's experience this method is unsatisfactory because it is difficult to know where to stop the distillation; in a high vacuum some material distils readily but the distillation can be continued to give further material which is not ethyleneimine (being comparatively non-volatile and odourless) and must consist of low polymers. Further, it is well known from other polymer systems that the complete removal of monomer from polymer by mere distillation is very difficult, so that the employment of a low vacuum, in which only ethyleneimine distils readily, would not solve the problem.

Jones *et al.* (*loc. cit.*) estimated conversions viscometrically and refractometrically. In each case the method was calibrated with solutions of poly(ethyleneimine), and possible changes in degree of polymerization (DP) with extent of reaction were neglected. In fact these changes are of the greatest importance, as will be shown later, and the viscometric method is therefore valueless. The extent to which the refractometric method applies cannot be stated in view of the lack of data on polymers of different degrees of polymerization, but it is likely to be reasonably sound.

In the present work reaction rates were followed dilatometrically. The dilatometers (below) were repeatedly washed with hot alcohol before use, attached to a high-vacuum line by standard ground joints, thoroughly pumped out, and weighed. Acid catalysts were introduced as solutions in a volatile solvent (chloroform, ether, or acetone) and the solvent was pumped off. Other materials (ethyleneimine, added amines, etc.) were distilled into the dilatometers *in vacuo*; known weights of water, *n*-butylamine, ethyleneimine dimer, etc. were taken from graduated capillary reservoirs. The dilatometers were sealed off and weighed (after completion of the kinetic measurements) together with the ground-joint "stump," thus obtaining the total weight of the contents. The weight of ethyleneimine was deduced by difference.

Readings at 40° were obtained by observing the meniscus with a cathetometer. From observations on very slow reactions it was concluded that the initial temperature equilibration in the thermostat was very rapid (*ca.* 1 min.) and the level of the meniscus at zero time could be obtained by extrapolation. For experiments at 100° the dilatometers were mounted in a glass "steam-tower" and continuous readings were taken; temperature equilibration was slower (*ca.* 10 min.) but since the rates were all very slow extrapolation to zero time was again easy. At higher temperatures a "vapour-tower," with different refluxing liquids, could be used, were it not for a tendency of an appreciable fraction of the dilatometers to explode. Therefore an initial reading of the meniscus-to-top distance on the dilatometer was taken in a bath at 25°, the dilatometer was then placed in a brass screw-cap tube and immersed in an oil-bath at 130° or 160° for a certain time, withdrawn, chilled, and returned to the bath at 25°; at least 6 hr. were then allowed for capillary drainage before the next reading. Serious errors arise without such drainage, particularly if the mixture is fairly viscous. (The reaction rate at 25° was shown to be negligible in these experiments).

For all runs in the presence of added substances, the volume change was calculated as a percentage of the initial volume of ethyleneimine only (not of the total volume).

*Calibration of Dilatometric Method.*—A Kjeldahl-type distillation was used. After a known volume contraction had occurred, the contents of the dilatometer were frozen into the bulb, which was cut off and dropped into approx. 40 ml. of *ca.* 0.1N-alkali. About 30 ml. of this solution were distilled into cold standard hydrochloric acid and the excess of acid was back-titrated (methyl-orange). Distillation of a further 5 ml. of the remaining solution gave no further basic material, so that the method has an advantage over "dry" distillation (see above). It is essential to distil from an alkaline solution, otherwise polymerization occurs during the distillation. As a check, known amounts of ethyleneimine were sealed in ampoules which were then broken under the solution to be distilled:

Contents of ampoule (mg.) .....	282	823	250	215
Solution from which distilled .....	H <sub>2</sub> O	H <sub>2</sub> O	0.1N-NaOH	0.1N-NaOH
Titre equiv. of distillate (mg.) .....	241	714	252	213
Recovery (%) .....	86	87	101	99

The end-point of the titration of ethyleneimine with dilute acid is quite stable at room temperature, but, on boiling, the solution becomes alkaline owing to the formation of 2-chloroethylamine (Gabriel, *Ber.*, 1888, 21, 1049).

Steam-distillations were carried out on a number of mixtures which had reacted under various conditions. The results are summarized in the Table. Though there is some experimental scatter it will be seen that the conversion factor *F* increases a little as the conversion increases; this was at first believed to be an artefact due to incomplete capillary



From the percentage conversion,  $100 [1 - (1 - p)^2]$ ,  $p$  is known. The percentage volume contraction can then be calculated, by assuming it to be proportional to  $p$  and taking the value of 9.3% contraction at 25° for  $p = 0.5$ , derived from the densities of monomer and dimer.\* In fact it was found that if a value of 10.0% contraction for  $p = 0.5$  was adopted instead (corresponding to a dimer density of 0.925), the calculated conversion factors agreed with the values experimentally determined at 25° within the estimated limits of the total experimental error (cf. Table).

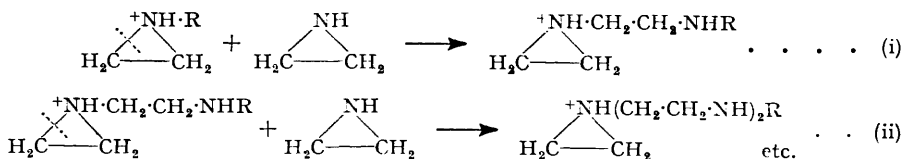
Results at 40°, of experiments with various acid catalysts, can be very well fitted in the same way as those at 25°, by taking 10% contraction for  $p = 0.5$ . A smaller number of measurements at 100° are also shown in the Table; these are more erratic, but can be reasonably interpreted in terms of a volume change of 12.5% at 100° for the conversion of monomer into dimer.

**Chromatographic Technique.**—Paper chromatograms were run downwards on Whatman No. 1 filter paper using butanol-acetic acid-water-pyridine (9 : 2 : 4 : 6). The spots were developed with ninhydrin, or with cobalt chloride-ninhydrin (Wiggins and Williams, *Nature*, 1952, 170, 279). With these reagents the various ethyleneimine polymers give purplish-mauve and salmon-coloured spots, respectively, with the exception of the dimer which gives a more yellowish-brown spot. The colours are presumably due to terminal  $\cdot\text{NH}_2$  groups, not to  $\cdot\text{NH}\cdot$  groups in the chain, since the ninhydrin-blue colour is developed with primary but not with secondary amines. Ethyleneimine itself gives no colour with ninhydrin, and piperazine [alleged by Jones *et al.* (*loc. cit.*) to be formed as a polymerization by-product] gives a very faint brownish spot. Amino-alcohols give deep reddish-purple spots.

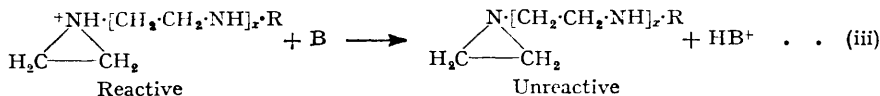
The dimer spot was identified by running a marker of the synthesized material, and the spots of successively lower  $R_F$  were taken to be trimer, tetramer, etc. A fresh chromatogram may reveal up to seven discernible spots or bands (*i.e.*, up to the octamer), with an unresolved "streak" of higher polymer. In addition, two very faint spots are sometimes found of higher  $R_F$  than the dimer spot; these were shown by markers to be caused by minute traces of ethanolamine and 2-amino-2'-hydroxydiethylamine (the hydrolysis product of the dimer), respectively.

## DISCUSSION

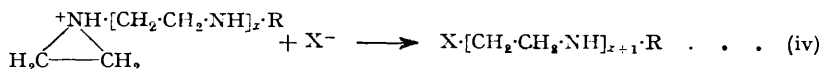
**Mechanism and Chromatographic Examination of the Reaction.**—Jones *et al.* (*loc. cit.*) suggested that the polymerization of ethyleneimine proceeded *via* ionic intermediates, thus :



In order to account for the catalysis by, for example, benzyl halides, it was assumed that R need not be H but could also be an organic radical. Termination (*i.e.*, deactivation of the reactive iminium ions) could occur either by proton abstraction :



(where B is any base, such as a monomer molecule, amino- or imino-nitrogen in a polymer, an anion, water, etc.) or by ring opening with an anion :



In reaction (iv), the place of  $\text{X}^-$  could, hypothetically, be taken by amino-nitrogen in a polymer molecule, the product then being a branched polymer-ion.

Two important implications of such a reaction scheme were overlooked by Jones *et al.* (*loc. cit.*). First, reaction (iii) should obviously be written as an equilibrium. The actual

\* The conversion of monomer into dimer corresponds to half the initial rings being opened, thus  $2\text{CH}_2\cdot\text{CH}_2\cdot\text{NH} \longrightarrow \overline{\text{CH}_2\cdot\text{CH}_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2}$ .

polymer-growth is relatively slow and protons will always be distributed amongst the various basic centres in the polymerizing mixture. If it is assumed that the basicities of the imino-nitrogen in the monomer and in the polymer molecule are similar, it follows that in the early stages of reaction most of the protons will be attached to monomer molecules and therefore most of the product will be dimer. Only as the dimer concentration becomes significant compared with the monomer concentration will appreciable quantities of trimer, tetramer, and higher polymers be formed. The mean degree of polymerization will rise throughout the reaction and towards the end all lower species such as monomer, dimer, and trimer will disappear. This has been confirmed from a series of chromatograms of the products of a reaction of ethyleneimine containing 3.6% of chloroacetic acid at 40°. Two drops of the reaction mixture were withdrawn at various times and dissolved in 0.1N-sodium hydroxide to stop the reaction; these samples were chromatographed. The approximate conversion was estimated by dilatometric measurements on an identical reaction mixture.

By analogy with the transfer reaction in vinyl polymerization (Flory, *J. Amer. Chem. Soc.*, 1937, **59**, 241), we may speak here of "transfer equilibrium." Its consequence is that while there are only a limited number of reactive centres, as in a vinyl polymerization, yet the degree of polymerization rises throughout the reaction, as in a polycondensation where all molecules have reactive groups. Further, the distribution of protons amongst the various species will only be a function of their relative concentrations and basic strengths; the molecular-weight distribution at a given conversion will be independent of the catalyst used or of its concentration, as is found experimentally. It is, of course, conceivable that similar transfer equilibria would operate in other types of ionic polymerizations, such as cationic vinyl polymerizations (cf. Pepper, *Quart. Rev.*, 1954, **8**, 88), but experimental evidence is lacking.

The second aspect not discussed by Jones *et al.* (*loc. cit.*) is the addition reaction of two poly(ethyleneimine) molecules. There is no reason why such a reaction should not occur, since it is no different in kind from the polymerization of other *N*-substituted ethyleneimines. Chromatograms show that this reaction of polymers with one another undoubtedly occurs, since prolonged reaction causes all low polymer species to disappear, though there would be insufficient monomer left for them to be converted into high polymers by addition of monomer only; furthermore, the self-polymerization of the synthesized "ethyleneimine-dimer" has been demonstrated by Jones *et al.* (*loc. cit.*). Some aspects of this matter, which bear on the general polymerization mechanism of *N*-substituted ethyleneimines, will be discussed in the following paper.

We shall consider a reaction mixture for which the following are assumed: (a) All ethyleneimine rings (whether monomeric or at the end of a polymer chain) are of equal reactivity. (b) All nitrogen atoms (*i.e.*, amino- and imino-centres) are of equal basicity; with this assumption the percentage of any particular basic species B present as BH<sup>+</sup> remains constant throughout a polymerization for a given total acid concentration, and the kinetic treatment is thereby greatly facilitated. (c) There is an instantaneous transfer equilibrium (as previously described) so that all imine rings can be regarded as having the same functionality, even though at any instant only a part of them will have protons attached.

On this basis the formal treatment of molecular-weight distribution becomes identical with Flory's (*loc. cit.*) (cf. p. 2567). In addition we shall also assume (d) that the catalyst concentration does not change significantly during the reaction. The formal treatment of polymerization *rates* then becomes very simple. The aspect of particular interest here is that the reaction is of the second order in "imine-rings" [cf. reaction (ii) and assumption (b)], and therefore

$$1/(1 - p) - 1 = p/(1 - p) = kt \quad . \quad . \quad . \quad . \quad . \quad (2)$$

By substitution from (1)

$$x^{-0.5} - 1 = kt \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The form of this equation is that for a reaction of order 1.5 with respect to monomer. [Though the molecular-weight distribution functions which obtain here are the same as

those developed by Flory (*loc. cit.*), the rate equations are not the same because of the chemical differences between the two systems.] Our kinetic results will be examined in relation to the scheme just discussed, to decide what modifications (if any) of the original assumptions must be made.

### KINETIC RESULTS

*The Catalytic Action of Water.—Preparation of dry ethyleneimine.* The ethyleneimine used in the early stages of this work was kept over freshly-cut sodium in a flask attached to the vacuum line, and was distilled *in vacuo* into a storage vessel next day. A certain irreproducibility in the results so obtained was attributed to varying amounts of water, and the ethyleneimine was subjected to additional drying. After standing over sodium for several days, the dry ethyleneimine was distilled *in vacuo* on to fresh sodium which had been heated *in vacuo*. If cooled by solid carbon dioxide the sodium slowly dissolved to give a deep blue solution; this colour must be related to that of solutions of sodium in liquid ammonia and of other alkali metals in certain simple aliphatic amines (cf. Moissan, *Compt. rend.*, 1899, 128, 26; Rengade, *ibid.*, 1905, 140, 246; 141, 196). On warming, the blue colour faded and hydrogen was evolved, the final product being, presumably, *N*-sodio-ethyleneimine; a yellowish-white

FIG. 1. Effect of drying of ethyleneimine on rate of polymerization at 130°.

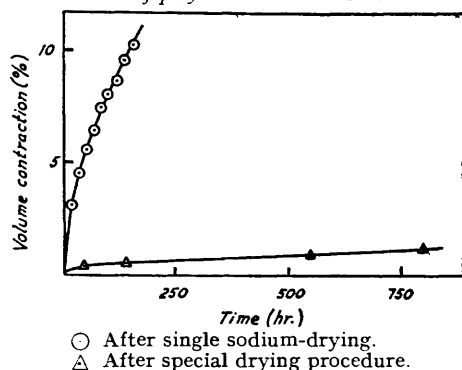
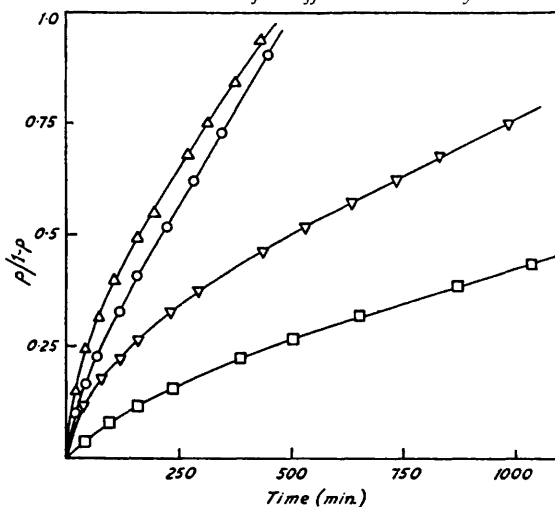


FIG. 2. Reaction course for different acid catalysts at 40°.



Concentrations in moles/1000 g. of mixture.  $\Delta$ , 0.625M-chloroacetic acid;  $\circ$ , 0.54M-toluene-*p*-sulphonic acid;  $\Delta$ , 1.00M-benzoic acid;  $\square$ , 0.88M-dichlorophenol.

powder is deposited if appreciable quantities of sodium are allowed to react. The ethyleneimine was allowed to dissolve sodium till some of the derivative was precipitated, and was then distilled *in vacuo* into another flask which had been carefully pumped out. It is significant that no blue colour with sodium was formed, even in the cold, if the ethyleneimine had not been subjected to the preliminary sodium-drying; the blue colour is evidently very readily destroyed by traces of water.

*Kinetic measurements.* Fig. 1 shows the course of reaction at 130° for ethyleneimine subjected to one sodium-drying only and for ethyleneimine treated by the special drying procedure. The removal of the last traces of water very greatly reduces the reaction rate, and it is likely, particularly in view of the reaction mechanism developed later, that perfectly dry ethyleneimine would not polymerize at these temperatures.

The curve for partially dried ethyleneimine in Fig. 1 is similar to those obtained with the specially dried ethyleneimine to which known small amounts of water (<5% by weight) had been added. A general feature of all these curves is that the initial reaction rate declines rapidly *before* a significant fraction of the ethyleneimine has been consumed. This is best shown by assuming that the reaction is of some particular order with respect to ethyleneimine monomer ( $x$ ) or unopened rings ( $1 - p$ ), and plotting the corresponding kinetic function which should be linear with time. The graphs are roughly linear for values of  $p$  above about 0.13,

*i.e.*, for monomer conversions greater than about 25%; below that value, the reaction rate is relatively much too fast and declines rapidly with increasing conversion. If the reaction is supposed to be of higher order, say second order in monomer, then the corresponding plot  $[(1 - p)^{-2} - 1]$  against  $t$  is again approximately linear, this time down to conversions of approximately 20%, but below that there is still a marked fast phase. (As will be shown, other acid catalyzts show a similar phenomenon.)

The possibility that the volume change observed in the fast phase of the reaction might be attributable to an initial conversion of water into ethanolamine,  $\overline{\text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}} + \text{H}_2\text{O} \longrightarrow \text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ , was considered. The volume change for this reaction calculated from the densities and volume changes on mixing is 28% of the volume of water reacting. This was found to bear no relation to the volume contraction in the initial fast phase, which seems practically independent of the water concentration. Further, chromatograms show that ethanolamine is formed only in minute traces.

Though the shape of the reaction curve is reproducible, the actual reaction rates varied by up to a factor of two, probably because during the long reaction times at the high temperatures involved traces of materials affecting the hydrogen-ion concentration are leached out of the glass; as will be shown, the reaction is catalyzed by hydrogen ions. Unsuccessful attempts were made to use silica dilatometers. These could be burnt out before use, but it appeared that ethyleneimine was afterwards very firmly adsorbed on the silica surface because charring always occurred on sealing off the dilatometers, even though the bulb was cooled in liquid air. The only generalizations possible are that the rate increases somewhat with increasing water concentration, and that rates at 100° are some 2–3 times less than those for corresponding mixtures at 130°. At 40° ethyleneimine containing 1% of water did not react detectably during several weeks.

In the presence of added acid catalyzts proved reproducible and detailed kinetic conclusions could be drawn.

*The Reaction catalyzed by Added Acids.*—The rate of polymerization of ethyleneimine in the presence of various acids was examined to ascertain the nature of the conversion–time curve, the dependence of rate on acid concentration, and the relative catalytic efficiency of the various acids. Five catalyzts, toluene-*p*-sulphonic acid ( $2 \times 10^{-1}$ ), monochloroacetic acid ( $1.5 \times 10^{-3}$ ), benzoic acid ( $6.5 \times 10^{-5}$ ), 2 : 4-dichlorophenol ( $3.1 \times 10^{-8}$ ), and phenol ( $1.3 \times 10^{-10}$ ) were used; the figures in parentheses are the appropriate dissociation constants  $K$  in aqueous solution at 25° (Heilbron and Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1943), except that for toluene-*p*-sulphonic acid no value was available and the acid was assumed to be of the same strength as benzenesulphonic acid. In aqueous solution the use of these acids would cover a wide range of hydrogen-ion concentrations. The corresponding  $K$ 's in ethyleneimine solution are not known but, if the various acids are all practically completely dissociated, equivalent concentrations should show similar catalytic effects. This expectation was only partially fulfilled.

*General features of the reaction, and evidence for consumption of catalyzt.* Fig. 2 shows the course of reaction for typical runs with four different acid catalyzts. The results are arbitrarily plotted according to equation (2). Two points are to be noted.

First, chloroacetic and toluene-*p*-sulphonic acids have similar catalytic activity, benzoic acid is less effective, and dichlorophenol less again, *i.e.*, the sequence is similar to that of the acid strengths in aqueous solution. Further, phenol, an even weaker acid, shows hardly any catalytic activity (cf. p. 2576); and water, which presumably promotes polymerization (at higher temperatures) by acting as an extremely weak acid, produces no detectable reaction rate at 40°. [It may be noted that water does not seem to be a necessary co-catalyzt for other acids, as appears to be the case with certain ionic vinyl polymerizations (cf. Pepper, *loc. cit.*); reactions catalyzed by chloroacetic or toluene-*p*-sulphonic acids were carried out with the specially dried ethyleneimine and with 3% of added water, and the reaction rates agreed within experimental error.]

Secondly, the reaction curves in Fig. 2 all show a progressively decreasing slope, the decrease being particularly pronounced in the early stages (cf. Fig. 1). This effect is definitely not due to some sort of physical adjustment, since ethyleneimine without a



catalyst does not show any volume change over long periods at 40°. It is therefore necessary to reject either assumption (b) or assumption (d) (see p. 2569) and assume instead (e) that the amino-nitrogen atoms in the polymer are of greater basicity than the imino-nitrogen atoms in monomer or polymer, and compete effectively for protons which would otherwise activate imino-rings, or (f) that the catalyst is consumed during the reaction. The rejection of assumption (a) does not help, since a considerable decline in rate takes place before more than a small fraction of the ethyleneimine has reacted (cf. Fig. 3).

Assumption (e) seems *a priori* unlikely; although ethyleneimine in aqueous solution is a weaker base than most aliphatic amines, the acid or basic character of a group in a polyacid or polybase is generally less pronounced than that of the same group in the monomeric analogue [*i.e.*, poly(ethyleneimine) would be a weaker base than, say, dimethylamine], and the range of basic strengths of substances in non-aqueous media is small compared with that in aqueous solutions (cf. Hall, *J. Amer. Chem. Soc.*, 1930, **52**, 5115). Nevertheless experiments were carried out. The chloroacetic acid-catalyzed polymerization of ethyleneimine in the presence of 10–15% of initially added bases (ethyleneimine

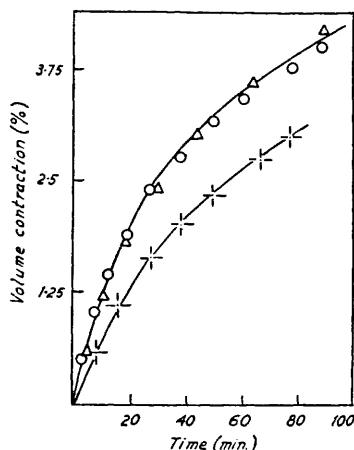


FIG. 3. Consumption of catalyst during reaction at 40°, with initially 3.2% (by wt.) of chloroacetic acid.

○, i; △, ii; +, iii (see below).

dimer, *n*-butylamine, or piperidine) was compared with a similar run in the absence of added amines. (If ethyleneimine is an abnormally weak base even in non-aqueous media, the addition of other bases should retard the reaction considerably.) Butylamine and piperidine showed only very small retarding effects which could be attributed to the dilution of the ethyleneimine. Fig. 3 shows the course of reaction, at the same initial acid concentration, for (i) ethyleneimine alone, (ii) ethyleneimine plus 10% of dimer, (iii) as (i) but recalculated by taking the new zero time as the time when 10% of ethyleneimine had been converted into dimer. If there were no destruction of catalyst, (ii) and (iii) should coincide. In actual fact, (i) and (ii) coincide reasonably but (iii) is much slower. It follows that the retardation in the early stages of reaction is not due to dimer formation but must be caused by a decrease in catalyst concentration.

This consumption of the acid catalyst is not surprising. It is known that hydrochloric and sulphurous acid, both of which polymerize ethyleneimine, can also give 2-chloroethylamine and taurine respectively (Gabriel, *Ber.*, 1888, **21**, 1049, 2664), and similar reactions can presumably occur with other acids. Jones *et al.* (*loc. cit.*) had already tentatively suggested that the consumption of acid was responsible for the rapid decrease of the polymerization rate in dilute hydrochloric acid.

To analyze the reaction rates further it is important to bear in mind that the molecular-weight distribution at a given conversion is independent of the nature or concentration of the acid catalyst; the relative distribution of protons amongst the various basic centres (*i.e.*, imino-nitrogen in monomer and polymer; primary and secondary aminonitrogen in polymer) is therefore also the same. Consequently at any given stage of conversion the

rate of reaction (between a charged and an uncharged imine-ring) will be proportional to the concentration of available protons.

We may write

$$-d[M]/dt = \sum_{x,y} k_{xy} [M_x] [M_y H^+] \dots \dots \dots (4)$$

where  $M_x$  represents an uncharged ethyleneimine-ring with a "tail" whose DP is  $(x - 1)$  and  $M_y H^+$  a charged ethyleneimine-ring with a "tail" of DP  $(y - 1)$ ;  $[M]$  represents the total concentration of imine-rings, both charged and uncharged. The ratio  $[M_y H^+] / \sum BH^+$ , where B is any basic centre, will be determined only by the extent of conversion of the reaction mixture, and is independent of the nature and concentration of the catalyst.

*Effect of initial acid concentration on reaction rate.* Results for four different acid catalysts at 40° are shown in Figs. 4—7. The percentage volume contraction is plotted against the function

$$[\text{time} \times \text{catalyst concentration (wt. \%)}] / (\text{dilution factor})$$

where the dilution factor =  $1 + (0.01 \times \text{the percentage concentration of catalyst})$ , is introduced as a rough compensation for the reduction in *initial* ethyleneimine concentration by the added catalyst; the factor was always less than 1.15.

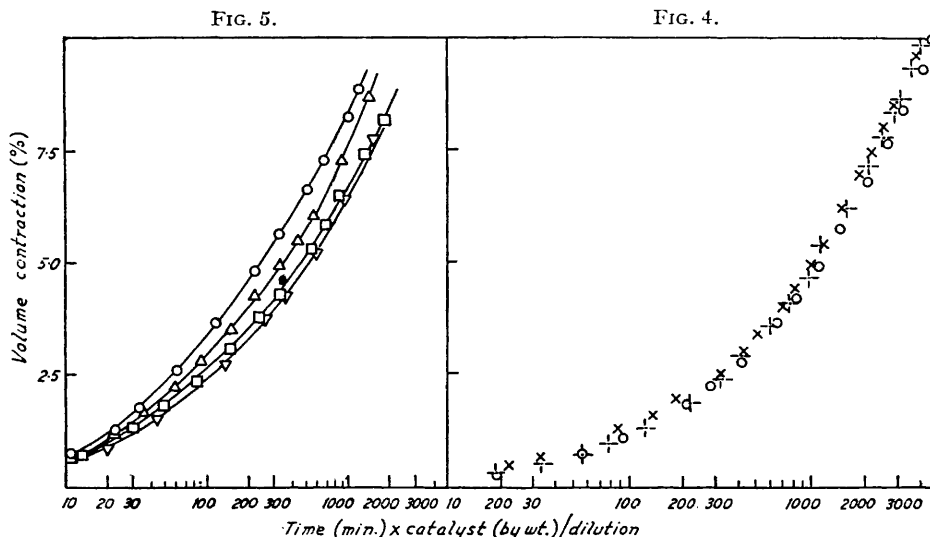


FIG. 4. Dependence of reaction rate on initial chloroacetic acid concentration at 40°.

○, 6.01%; △, 3.85%; □, 2.30%; ▽, 1.30% (by weight).

FIG. 5. Dependence of reaction rate on initial toluene-p-sulphonic acid concentration at 40°.

○, 9.23%; +, 3.81%; ×, 0.75% (by weight).

(a) *Toluene-p-sulphonic acid.* Fig. 5 shows that results obtained over a 13-fold variation in initial toluenesulphonic acid are very satisfactorily represented by a single curve, so although catalyst is consumed during the reaction, the rate is at all times proportional to the initial acid concentration  $[HA]_0$ :

$$-d[M]/dt \propto [HA]_0 \dots \dots \dots (5)$$

The similarity in catalytic activity of chloroacetic and toluene-*p*-sulphonic acid (Fig. 2) suggests that both these acids are practically completely ionized in ethyleneimine. Consequently  $\Sigma[BH^+] = [HA]$ , the acid concentration at time  $t$ . Now as  $[M_y H^+] / \Sigma[BH^+]$  is independent of acid concentration

$$[M_y H^+] \propto [HA] \dots \dots \dots (6)$$

and from (4) and (6),

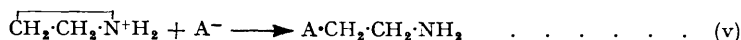
$$-d[M]/dt \propto [HA] \dots \dots \dots (7)$$

*i.e.*, the rate at time  $t$  is proportional to the acid concentration at that moment. For (5) and (7) to hold simultaneously, the fractional decrease in acid concentration must bear a constant ratio to the fractional decrease in monomer concentration  $[M]$ , *i.e.*,

$$\frac{1}{[M]} \frac{d[M]}{dt} / \frac{1}{[HA]} \frac{d[HA]}{dt} = K \quad \dots \quad (8)$$

Combining (7) and (8), we have  $-d[HA]/dt \propto [HA]^2$   $\dots \dots \dots$  (9)

This second-order dependence accords with a consumption of acids by the reaction



and by analogous reactions of  $\text{A}^-$  with polymer cations. From (v),

$$-d[HA]/dt = \sum_y k_{y, \text{A}^-} [\text{A}^-] [\text{M}_y \text{H}^+] \quad \dots \dots \dots (10)$$

Now  $[\text{A}^-] = [\text{HA}]$  and  $[\text{M}_y \text{H}^+] \propto [\text{HA}]$ ; therefore, from (10), equation (9) follows. We conclude that the kinetics of the polymerization catalyzed by toluene-*p*-sulphonic acid are

FIG. 6. Dependence of reaction rate on initial benzoic acid concentration at 40°.

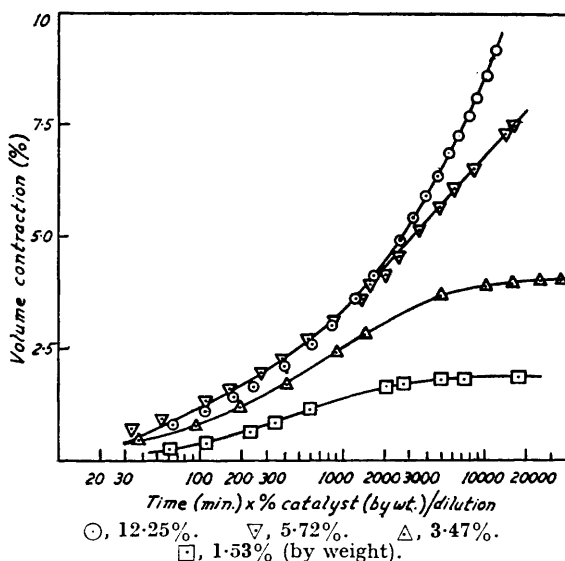
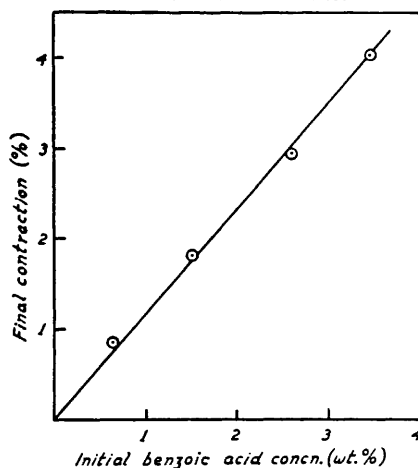


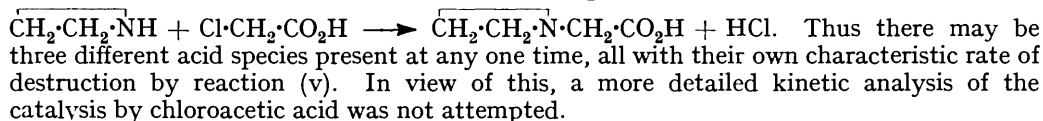
FIG. 7. Total amount of reaction at low benzoic acid concentrations.



fully understandable in terms of acid consumption by reaction (v), giving products analogous to those prepared with hydrochloric and sulphurous acid (cf. p. 2572).

The observations by Jones *et al.* (*loc. cit.*) that the hydrochloric acid-catalyzed polymerization is of an apparently very high initial order with regard to ethyleneimine but that the half-life is inversely proportional to the initial acid concentration, are exactly analogous to the present (more detailed) results on the toluene-*p*-sulphonic acid system. There is little doubt, therefore, that the same explanation of the kinetics holds in both cases, particularly as in the hydrochloric acid case 2-chloroethylamine is known to be formed [cf. reaction (v)].

(b) *Chloroacetic acid.* Fig. 4 shows results over an approximately five-fold range of chloroacetic acid concentrations, plotted in the same way as in Fig. 5. The state of affairs is less simple than for toluene-*p*-sulphonic acid, as the rate is somewhat more than first-order with regard to initial acid concentration. A complicating factor is the possible reaction



(c) *Benzoic acid.* Fig. 6 shows the dependence of rate on initial benzoic acid concentration. Here the state of affairs is strikingly different from that in Figs. 4 and 5 and the overall rate is clearly greater than first order with respect to initial acid concentration. The divergence is particularly pronounced in the later stages of reaction, where the runs at low benzoic acid concentration practically stop even though most of the ethyleneimine has still not reacted. The final total amount of reaction can, in these cases, be accurately estimated and is accurately proportional to the initial acid concentration (see Fig. 7).

In attempting to explain the results in Figs. 6 and 7, it is necessary also to recall the data of Fig. 2, showing that the catalytic action of benzoic acid is much less than that of stronger acids, even in the initial stages of reaction. For the stronger acids we have

assumed complete dissociation, thus *e.g.*,  $\overline{\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}} + \text{HA} \longrightarrow \overline{\text{CH}_2\cdot\text{CH}_2\cdot\text{N}^+\text{H}_2} + \text{A}^-$ . To account for the lower catalytic activity of a weak acid, we may write the above reaction as an equilibrium, and assume a considerable amount of undissociated HA to be present;

or we can assume that with a weak acid an ion-pair complex (II) rather than free ions are formed, and that the catalytic activity of such an ion-pair (*i.e.* its tendency to ring-rupture) is less than that of a free iminium ion. The possibility of such ion-pairs' participating in ionic vinyl polymerizations has been discussed occasionally (cf. Pepper, *loc. cit.*, p. 103).

Various reaction schemes based on the first of these assumptions were examined, but none explained the simple linear result in Fig. 7; introduction of an equilibrium generally produces a square-root dependence. On the other hand, the results of Figs. 6 and 7 are readily understood in terms of the second assumption, assuming further that the equilibrium lies completely over to the ion-pair side. For  $-d[\text{M}]/dt$  the treatment is then exactly analogous to that for toluene-*p*-sulphonic acid, the concentration of free iminium ions simply being replaced by the concentration of ion-pairs, and equation (7) holds. However, the destruction of catalyst, which was previously a second-order reaction (v), now becomes a first-order reaction of the ion-pair, and therefore

$$-d[\text{HA}]/dt \propto [\text{HA}] \quad \dots \quad (11)$$

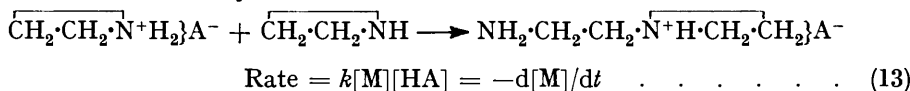
Consequently equation (8) for strong acids is replaced for weak acids by

$$\frac{1}{[\text{M}]} \frac{d[\text{M}]}{dt} / \frac{1}{[\text{HA}]} \frac{d[\text{HA}]}{dt} = K[\text{HA}] \quad \dots \quad (12)$$

According to equation (12), the fractional decrease in catalyst concentration (and hence in rate) relative to the fractional decrease in monomer concentration would be greater the lower the acid concentration; in other words, the initial rate would decline most rapidly for the most dilute acid solution, as is the case in Fig. 6.

With regard to the limited total amount of reaction ( $\Delta[\text{M}]$ ) occurring at very low benzoic acid concentrations (Fig. 7), we assume that, because the conversion of ethyleneimine is very small, reactions of polymeric products can be neglected. We then have:

(i) Monomer consumed by



where  $[\text{HA}] = \text{total acid concentration} = \text{concentration of ion pairs}$ .

(ii) Acid consumed by  $\overline{\text{CH}_2\cdot\text{CH}_2\cdot\text{N}^+\text{H}_2}\text{A}^- \longrightarrow \text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{A}$

$$\text{Rate} = k'[\text{HA}] = -d[\text{HA}]/dt \quad \dots \quad (14)$$

Hence

$$d[\text{M}]/d[\text{HA}] = k[\text{M}]/k' \quad \dots \quad (15)$$

Since  $[\text{M}]$  remains practically constant in the experiments of Fig. 7, we have from (15)

$$\Delta[\text{M}]/\Delta[\text{HA}] = k'' \quad \dots \quad (16)$$

As all the acid is finally consumed, it follows from (16) that

$$\Delta[M]_{t \rightarrow \infty} = k''[HA]_0 \quad \dots \quad (17)$$

*i.e.*, the total monomer consumption is proportional to the initial acid concentration, as found (Fig. 7).

It is concluded that the assumption of ion-pairs rather than of free ions fully explains the differences in kinetic behaviour between the strong toluene-*p*-sulphonic acid and the weak benzoic acid. It is possible that the data in Fig. 5 indicate chloroacetic acid to be an intermediate case.

(d) *2 : 4-Dichlorophenol*. In aqueous solution this is an even weaker acid than benzoic acid. Fig. 8 illustrates its catalytic effect on the polymerization of ethyleneimine, plotted as for the other acids. The rate is slower than with an equivalent concentration of benzoic acid (cf. Fig. 2), but the nature of the reaction curves is the same (cf. Figs. 6 and 8), and the interpretation suggested for benzoic acid presumably applies, with different velocity constants, to *2 : 4*-dichlorophenol also.

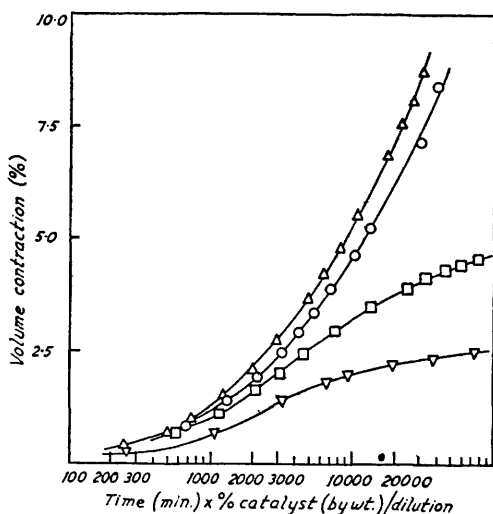


FIG. 8. *Dependence of reaction rate on initial 2 : 4-dichlorophenol concentration at 40°.*

- △, 14.3%.
- , 8.55%.
- , 4.52%.
- ▽, 2.17% (by weight).

(e) *Phenol*. Early experiments employing phenol proved very irreproducible. A stock solution of phenol in chloroform was used; the reaction rate at a given phenol concentration, though always very slow, increased with the age of this solution. This effect was ascribed to the production of hydrogen chloride by decomposition of the chloroform; traces of this strong acid would give pronounced effects compared to the very slight activity of phenol. In confirmation, the use of stock solutions of phenol in ether gave reproducible rates which were somewhat lower than if a freshly prepared chloroform solution was used, and much lower than if the solution in chloroform was old.

No comparable difficulty was encountered with other acid catalysts; ether, acetone, and chloroform solutions all gave similar results. Phenol is a particularly unfavourable case in that its catalytic activity is very slight (at 40° ethyleneimine containing 9% of phenol contracts by 1.4% in 300 hrs. compared with 90 min. for *2 : 4*-dichlorophenol). Further, the material separates as a liquid when the solvent is pumped off, and is therefore more likely to retain hydrogen chloride than a crystalline acid residue would be.

The detailed kinetics of the phenol-catalyzed reaction were not examined.

*The results of Kern and Feuerstein (loc. cit.).* Two phenomena observed by these authors (cf. p. 2564) require brief mention here. First, an examination of their rather limited data on the reaction in the presence of sulphanic acid show a reaction course very similar to that observed here with toluene-*p*-sulphonic acid. Secondly, the explosive course of the reaction at high temperatures and catalyst concentrations is almost certainly due to inadequate dissipation of the heat of polymerization at high rates of reaction.

*Summary.*—Although the polymerization of ethyleneimine is an addition polymerization, it differs from a vinyl addition polymerization (radical or ionic) in two fundamental respects. First, the existence of a “transfer equilibrium” entails that all monomer *and polymer* molecules are potentially capable of activation or deactivation, and thus produces certain kinetic features similar to those of condensation polymerizations. Secondly, the fractional consumption of catalyst is generally greater than that of monomer, whereas in other polymerizations the reverse tends to be the case; the detailed kinetics of monomer conversion are therefore largely determined by the kinetics of catalyst destruction, and hence may vary from one catalyst to another.

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