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The Kinetics of Epoxy Polymerization*

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SUMMARY

The rate of polymerization of a diepoxide and a dicarboxylic acid anhydride with a tertiary amine catalyst has been explored. Molar ratios of epoxy to anhydride in the range from 10 : 1-0.8 : 1 were investigated in a temperature range of 60-120°C. The observed reaction rate may be expressed by the following rate equation:

$$\frac{(\text{d epoxy})}{(\text{dt})} = 2.5 \times 10^{-5} \exp(-6600/RT)\ \text{min}^{-1}\,[\text{Cat}]^{-1}$$

The rate was clearly first-order in catalyst, but appeared to be zero-order in epoxy and anhydride, for the ratios of epoxy and anhydride investigated. The analysis of the kinetic data indicated that the rate-controlling step was the activation of the catalyst. This was interpreted in terms of the reaction of catalyst with cocatalyst to form an activated species. This mechanism is consistent with available data and with the fundamental chemical requirements for epoxy polymerization. The proposed mechanism of reaction adequately describes the activation, initiation, propagation, and termination steps of the polymerization reaction.

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INTRODUCTION

The purpose of this investigation was to explore the kinetics and resolve the mechanism of a particularly useful example of the amine-catalyzed reaction between an anhydride and diepoxide to form a polymer. The specific reaction in question is the polymerization of the diglycidyl ether of bisphenol A (DER 332) with methyl nadic anhydride (MNA) catalyzed by benzyldimethylamine (BDMA).

Although much work has been done with model compounds, in recent years only limited effort has been expended on studies with commercially available materials. With the particular system of interest, two studies have been performed, which appear to be carefully conceived but nevertheless lead to contradictory conclusions [1, 2]. Fischer [1] carried out a study of the kinetics of the reaction between DER 332 and MNA catalyzed by BDMA. He observed that the rate of disappearance of DER was dependent neither on the DER concentration nor on the concentration of MNA, but only on the catalyst. Yet the subsequent analysis of the data and postulated mechanism were not consistent with observed zero-order dependence of the reaction on the major components.

A more recent study by Tanaka and Kakiuchi [2] was interpreted as indicating first-order dependence of the reaction rate on each of the major components. A critical analysis of the data suggests, however, that these conclusions were not entirely warranted, since the data did not fit a second-order equation.

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EXPERIMENTAL

Reagents and Reactants

The materials used for analysis were reagent grade; chloroform, ACS grade; tetrabutylammonium iodide solution, (20%) w/v 20 g; TBAI (EK White Label 4702) dissolved in chloroform and diluted to 200 ml.

$HClO_4$ (0.1 N in glacial acetic acid): 8 ml of 61% $HClO_4$ were mixed slowly into 800 ml of glacial acetic acid in a 2-liter beaker. Then 25.4 ml of acetic anhydride were added slowly while stirring. The beaker was kept in a cold water bath to avoid temperature rise during pregnation. Then the solution was diluted with glacial acetic acid to 1 liter.

Crystal violet indicator solution: 0.1% in chloroform. All polymer reactants were commercially available: DER 332 was obtained from Dow Chemical Co., MNA from Allied Chemical Co., and BDMA from Miles Chemical Co.

General Procedure

A quench-chemical analysis technique was selected over other possible techniques, such as continuous, in situ, IR analysis [3], dilatometry, or differential thermal analysis, because preliminary studies indicated that, otherwise, there would be some ambiguity in interpretation of the data. The chemical analysis techniques employed are similar to the ones described by Tanaka and Kakiuchi [2] with some refinements in procedure.

In preliminary exploratory runs, it was found that samples of the reaction mixture could easily and rapidly be quenched by cooling to dry-ice temperatures and maintained in a nonreactive condition by storing in a freezer (–20°C). Warming the samples to room temperature for analysis did not affect the accuracy of the results.

Ten milliliters of chloroform were added and the samples were dissolved by swirling the flask. Then 10 ml of tetrabutylammonium iodide solution and three drops of crystal violet indicator solution were added. The solution was titrated rapidly, with continuous swirling, with 0.1 N $HClO_4$ titrant until near the equivalence point. The end point was reached with the first persistent green color (30 sec or longer), obtained when only one drop of titrant changed the color of the solution from blue to green. Some care had to be exercised in this observation because the end point has a tendency to drift or fade.

The 0.1 N $HClO_4$ titrant was standardized in a similar manner against the pure epoxy (DER 332) in terms of millimoles of epoxy per weight of $HClO_4$ titrant. With the pure epoxy DER 332 alone (in the absence of the acid anhydride and catalyst), the change from blue to green was not so sharp, and the sharp change from purple to blue was more sensitive.

Detailed Kinetic Measurement Procedure

The epoxide and acid anhydride were weighed to ±0.1 g, directly into a tared three-neck, 500-ml Pyrex glass reaction flask on a triple-beam balance. All runs had approximately the same batch weight of about 120 g. One neck was open to the atmosphere through a drying tube containing desiccant. The center neck, with airtight seal, was used for a variable-speed, motor-driven glass-Teflon stirring paddle. The third neck was used to insert glass tubing to pipet samples and was kept stoppered except during sampling. The reaction mixtures were mixed thoroughly and vigorously without splattering, except briefly during sampling, by controlling the speed of the submerged paddle.

The reaction flask was immersed, except for the neck openings, in a constant-temperature, vigorously stirred oil bath. The temperature of the reaction mixture for these slow reactions was essentially the same as the bath temperature throughout the run. As soon

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as the epoxide-acid anhydride mixture was a homogeneous solution and at thermal equilibrium with the bath (about 5-10 min), duplicate samples were removed. The catalyst was added from a hypodermic (stainless-steel needle), and duplicate samples of the mixture were obtained after 3 min of thorough mixing. Samples were taken at sufficient preselected intervals, before estimated gelation, to obtain generally about 10 samples or time intervals.

Convenient lengths (20 cm) of Pyrex glass tubing (7 mm) that had partially restricted tips and were marked to deliver about 0.3-g samples in sufficient number (i.e., 20) were used with a rubber bulb for pipetting individual samples of each run. Each sample was quickly transferred to a tared 125-ml Pyrex Erlenmeyer flask and sealed tightly with a rubber stopper. The flask was then immediately quenched in an acetone-dry ice bath and transferred to a freezer (–20°C). Just before analysis (within 24 hr) each flask (duplicate samples) was removed from the freezer and weighed at room temperature to obtain the weight of sample.

RESULTS AND DISCUSSION

The reaction between the epoxy resin (DER 332) and the acid anhydride (MNA) in the presence of an amine catalyst (BDMA) was investigated at constant temperatures of 32.0, 60.5, 93.5, 108, and 121°C, and at molar ratios of epoxy/MNA varying from 10 to 0.8. The extent of cure with time was established from the extent of reaction of the epoxy resin. Samples of each mixture were obtained at intervals during the reaction.

The results of kinetic runs are summarized in Figs. 1-5. From Fig. 1 it is clear that the rate of disappearance of epoxy is not affected by changes in the epoxy concentration. Figure 2 indicates that the rate of disappearance of epoxy is directly proportional to the catalyst concentration; this is indicative of a first-order dependence. This is further illustrated by Fig. 3, where various ratios of epoxy to MNA are used, and by Fig. 4, where constant composition, but different temperatures are maintained. It is also clear from Fig. 4 that at zero catalyst concentration, reaction can still occur, albeit at a greatly reduced rate.

The data in Fig. 3 indicate that the reaction is zero-order not only in epoxy but also in MNA, since in none of these cases is the rate of disappearance other than constant. The only apparent exception is the top curve of Fig. 3 where, in fact, the initial and subsequent curves have constant slopes and the break in the curve occurs where calculations indicate that one of the components is entirely consumed. It is interesting to note that the rate beyond this point is of the same order of magnitude as that for zero catalyst concentration (Fig. 3).

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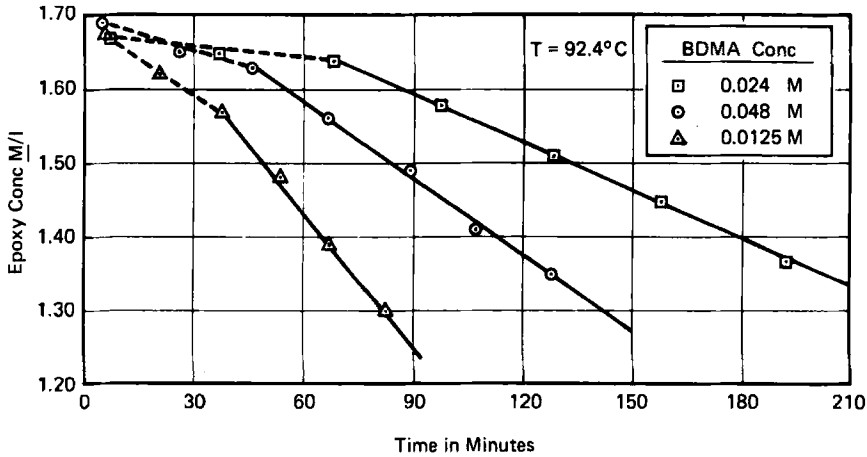

Fig. 1. Effect of catalyst concentration on rate.

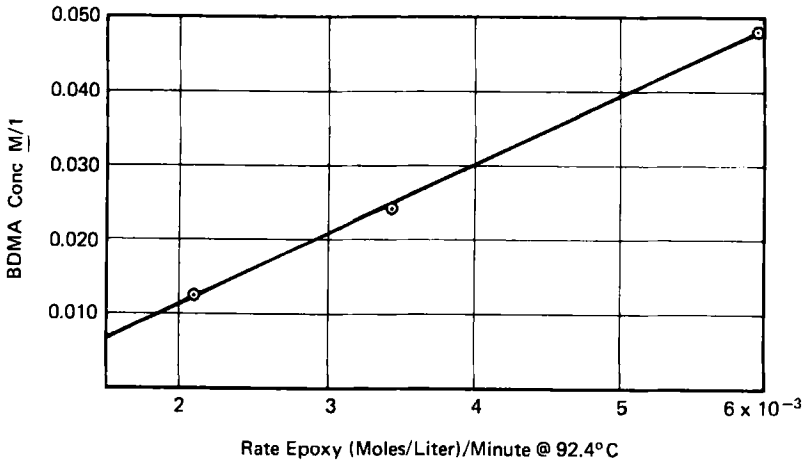

Fig. 2. Rate dependence on catalyst concentration.

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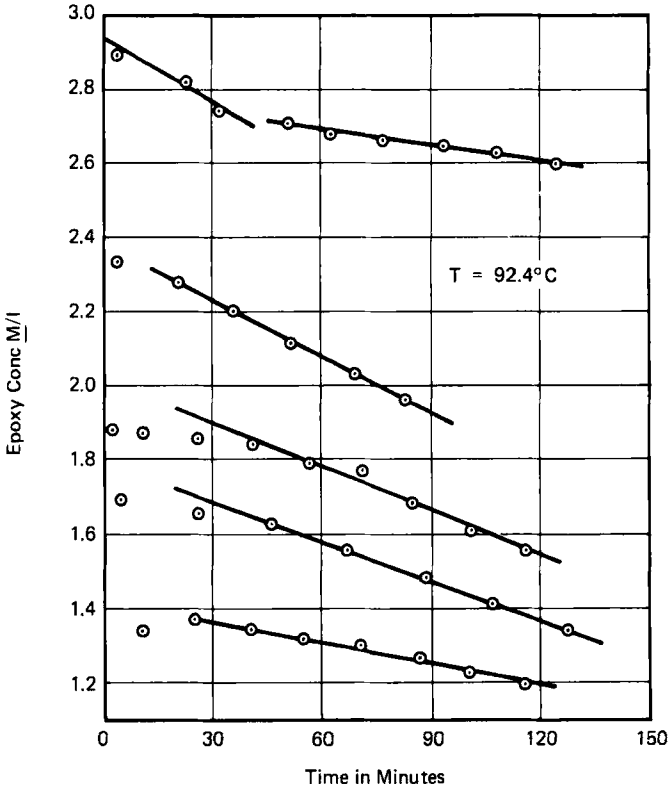

Fig. 3. Effect of epoxy concentration on reaction rate.

The apparently slower rate in the lower four curves of Fig. 3 during the first 20 min of reaction is due to some ambiguity in the determination of the epoxy concentration. During the first 20 min there is some temperature lag and there may also be a mixing effect. Both of these effects would tend to interfere with the rate of the reaction.

Additional confirmation of the independence of the rate upon any component except the catalyst is evidenced by the calculated rate constants shown in Table 1. It is obvious that the calculated rate constants demonstrated are all approximately the same. This would not have been the case had either the epoxy or MNA had an effect upon the rate of disappearance of the epoxy. This suggests that a low-velocity reaction is occurring with epoxy which is, however, independent of the catalyst added and does not involve addition to MNA. The temperature-dependent rate data of Fig. 4, when plotted in the appropriate manner, generate the typical Arrhenius plot from

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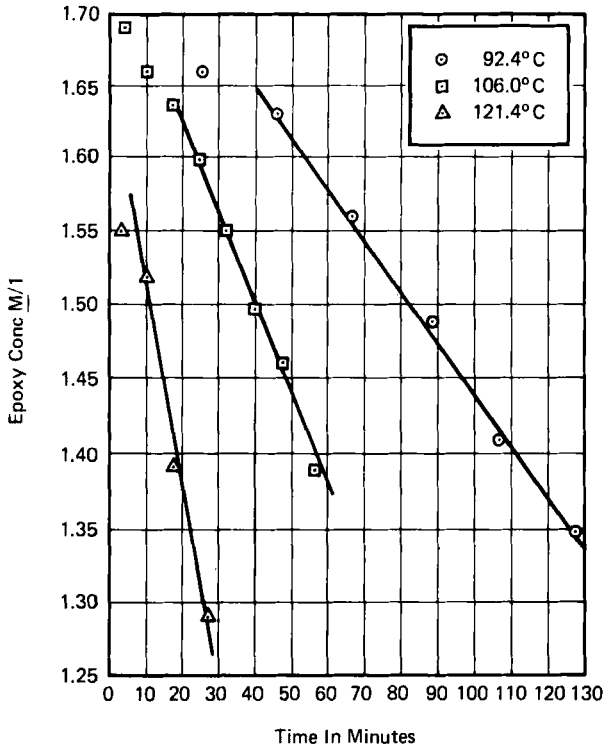

Fig. 4. Effect of temperature on reaction rate.

which an activation energy of 6.6 kcal and a pre-exponential term of 2.5×10^{-5} min^{-1} are determined. The kinetics of the reaction can thus be expressed in terms of the rate of disappearance of DER. The rate expression is

$$\frac{d(DER)}{dt} = k(DER)^0(MNA)^0(BDMA)^1$$

where

$$k = 2.5\ 10^{-5} \exp(-6600/RT)\ min^{-1}$$

In the attempt to elucidate the detailed mechanism of the reaction, a set of equations which describe the kinetic sequence was developed. This sequence is reproduced below.

For convenience, let the concentrations of the catalyst, DER, and MNA be represented by the letters C, A, and B, respectively. Then

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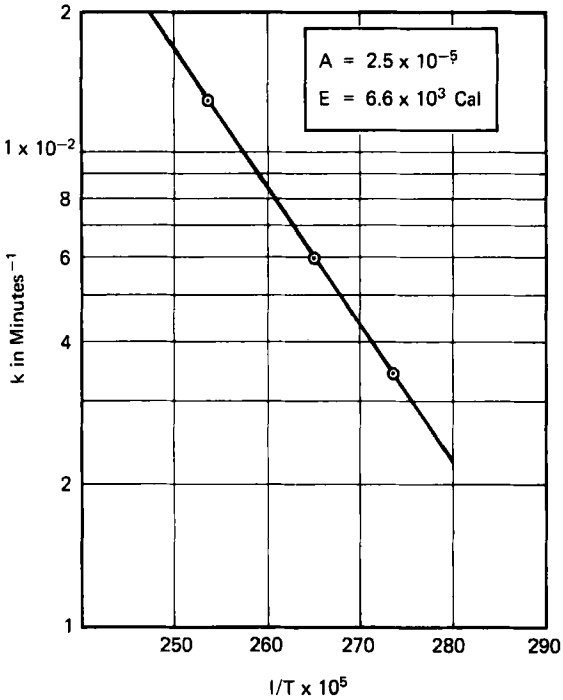

Fig. 5. Arrhenius plot.

Table 1. Dependence of Rate Constants on Catalyst Concentration

Run no.	Concentration, moles/liter DER	MNA	BDMA × 10^2	Rate × 10^3, moles $liter^{-1}$ min^{-1}	k^a × 10^1, sec^{-1}
4	1.69	3.03	2.40	3.43	1.43
7	2.85	0.564	4.07	5.73	1.41
8	2.36	1.63	3.36	4.95	1.47
9	1.94	2.49	2.79	3.86	1.38
10	1.44	3.55	1.35	1.83	1.36

Average 1.41 ± 0.04

[a]k calculated from rates established by the kinetic data plots and from the assumption that the catalyst (BDMA) was the determinative species.

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assume that the catalyst is involved in an activation step where k_1 is rate-determining.

$$C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C^* \tag{1}$$

Then let C* react rapidly and irreversibly with A

$$C^* + A \xrightarrow{k_3} (CA)^* \tag{2}$$

and subsequently with B

$$(CA)^* + B \xrightarrow{k_4} (AB)^* + C \tag{3}$$

The sum of these reactions gives

$$A + B \longrightarrow (AB)^*$$

It then may be assumed that (AB)* can further react to form $(AB)_n$ in fast reactions to yield the final products. However, Eqs. (1)-(3) suffice to express the controlling mechanisms of the reaction. If one writes the usual differential equation for the rates of disappearance of the species (A), (B), and (C), the following equations result:

$$\frac{-dC}{dt} = k_1C - k_2C^* - k_4(CA)^*(B) \tag{4}$$

$$\frac{-dA}{dt} = k_3(C^*)(A) \tag{5}$$

$$\frac{-dB}{dt} = k_4(CA)^*B \tag{6}$$

and

$$\frac{-dC^*}{dt} = k_2C^* + k_3C^*A - k_1C \tag{7}$$

$$\frac{-d(CA)^*}{dt} = k_4(CA)^*B - k_3(C)^*A \tag{8}$$

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Applying the steady-state assumption that

$$\frac{-dC^*}{dt} = \frac{d(CA)^*}{dt} = 0.$$

Setting

$$\frac{-dC^*}{dt} = 0$$

and solving for C* in Eq. (7) permits one to substitute the results into Eq. (5) which gives

$$\frac{-dA}{dt} = k_3 \frac{k_1 CA}{(k_2 + k_3 A)} \tag{9}$$

If, now, k_3A is much larger than k_2, Eq. (9) becomes

$$\frac{-dA}{dt} = k_1 C \tag{10}$$

using

$$-d(CA)^*dt = 0$$

and then solves Eq. (8) for (CA)* and substitutes into Eq. (6), the same development and arguments apply to the rate of disappearance of B to yield

$$\frac{-dB}{dt} = k_1 C \tag{11}$$

Thus

$$\frac{-dB}{dt} = \frac{-dA}{dt} = k_1 C \tag{12}$$

this has been observed experimentally (i.e., the rate of disappearence of DER and MNA does not depend on the concentration of either species but rather on the concentration of the catalyst).

Since it appears that catalyst activation can provide an explanation of the observed kinetics, it is worthwhile to speculate on how this could occur. The alternatives which present themselves are dissociation, racemization, rearrangement, or (as is actually believed to be the case), participation with small (trace) amounts of impurity cocatalyst present in one or another of the major components. With the first three alternatives, it is difficult to visualize what the activated species might be, but there is much evidence to support the speculation of an impurity cocatalyst. Other examples

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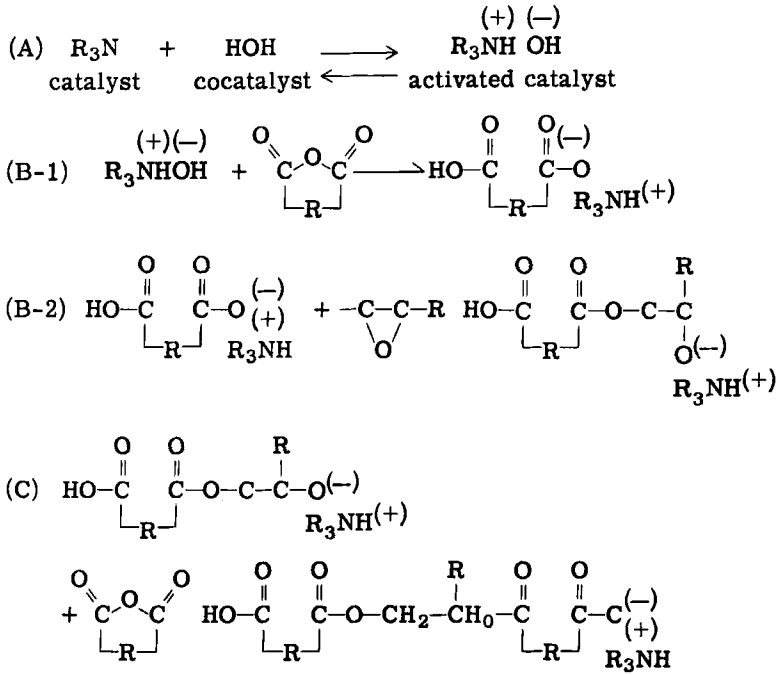
of this effect are well documented (e.g., $AlCl_3$ in Friedel-Crafts reactions active in the presence of trace amounts of water). The activation energy evaluated for this reaction is of the same order of magnitude observed for other catalyst-cocatalyst reactions [4]. If the postulate of cocatalysis is correct, the rate-determining step is a pseudo first-order reaction where the cocatalyst species was not observed. Thus, the rate-determining step should be more correctly written

$$\text{Cat} + \text{Co} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (\text{Cat Co})$$

The data presented have indicated a kinetic sequence for the tertiary amine-catalyzed epoxy-anhydride polymerization which is first-order in catalyst and zero-order in epoxide and anhydride. The following mechanism is presented as being consistent with the experimental rate equation and is shown later to explain other apparently anomalous phenomena.

The mechanism consists of four discrete steps: (A) catalyst activation, (B) chain initiation, (C) chain propagation, and (D) termination. These steps may be represented as follows:



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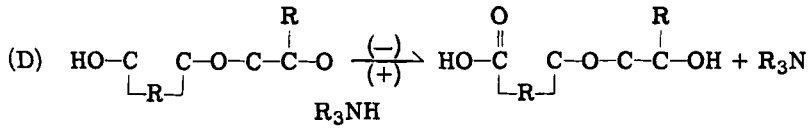

In step A, the amine catalyst is activated by reaction with a cocatalyst to form a quaternary salt. The cocatalyst may be such species as water, phenol, alcohol, or acid. All of these species may appear as impurities or contaminants in the epoxy or anhydride substrates. The energy of activation calculated for the rate-controlling substrates. The energy of activation calculated for the rate-controlling step of the reaction was 6.6 kcal. It is postulated that the amine-cocatalyst reaction to form a quaternary salt is the rate-controlling step in the sequence shown above.

In step B, chain initiation occurs by the fast reaction of the quaternary salt with anhydride to give the carboxy anion carboxylic acid moiety. The anion then reacts with an epoxy molecule to yield an ester alkoxide anion as shown in step B-2.

In step C, the reaction is propagated by the further reaction of alkoxide ion with anhydride to generate a second ester carboxy anion, etc.

Step D, the termination step, occurs when the anion, instead of reacting with another epoxy or anhydride molecule, abstracts the proton from the quaternary amine and regenerates deactivated catalyst together with a neutral terminal group on the growing polymer chain.

The regenerated tertiary amine may react with more cocatalyst and start another polymer chain.

Previous work by Fischer [1] had also indicated a zero-order dependence on epoxy and anhydride concentration, and first-order dependence on catalyst. However, the mechanism presented did not fit the kinetic sequence demanded by the zero-order dependence. Other attempts to define the mechanism of the epoxy anhydride reaction presented similar mechanistic approaches [5]. Examination of the mechanisms suggested by Fischer [1], Tanaka and Kakiuchi [2], and Lee and Neville [5] indicated that all were similar regardless of the fact that Tanaka and Kakiuchi had postulated a second-order reaction and Fischer a first-order reaction in catalyst only.

A serious drawback to the mechanism as presented by Fischer [1], Tanaka and Kakiuchi [2], and Lee and Neville [5] is that as the chain propagates there is a continually increasing separation of charges (i.e., the mechanism indicated the formation of a positive center by the reaction of amine catalyst with anhydride and as the anion portion reacted first with epoxy then with anhydride, the negative charge was carried further and further from the positive center).

In addition to the requirement for further and further charge separation demanded by this sequence, none of the investigators

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has been able to clearly define a termination step which results in neutral species.

To summarize briefly, a kinetic sequence for the polymerization of an epoxy-anhydride-tertiary amine system has been presented. The postulated mechanism fits the zero-order equation derived and also provides a reaction path not subject to the limitations inherent in previous work (namely, the requirement for charge separation and the inability to define a logical termination step for the growing chain). The basic concept presented is that the rate-controlling step is the activation of the tertiary amine catalyst by reaction with a cocatalyst to form a quaternary salt. Evidence to support this thesis is provided by the activation energy of 6.6 kcal for the reaction, which compares favorably with the 6.3 kcal activation energy for the formation of quaternary salts. Quaternary salts have been shown to be active in initiating epoxy-anhydride polymerization reactions [6]. It has been noted by several workers that small amounts of water, alcohols, or acids measurably increase the rate of epoxy polymerization in the presence of amine catalysts [7-9].

It is planned to obtain corroboration of the proposed mechanism by several experiments. One experiment would be to use highly purified materials which are anhydrous so that no cocatalyst is available for activation of the amine. It should be noted in this regard that activation of the amine by a hydroxyl group in the epoxy molecule is excluded by the kinetic sequence. If such activation made an appreciable contribution to the mechanism, then the concentration of epoxy would enter into the rate equation since the concentration of hydroxyl groups would be directly related to the concentration of the epoxy compound.

Some evidence would also be gained by determination of the rate in solvents of varying dielectric constants. Solvents with a high dielectric constant would tend to favor the reaction by aiding formation of the quaternary salts, and low dielectric constant solvents would depress the reaction rate. However, it is possible that such data would be somewhat ambiguous, since epoxy reactions are generally represented as ionic in nature and dielectric media would therefore exert similar influences. One final experiment would be to perform the study again with highly purified materials using a quaternary salt as the catalyst instead of the tertiary amine. Any difference in rate between the pure materials and tertiary amine and the pure materials and quaternary salt would be directly related to the difference in the mechanism of the reaction.

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