Kinetics of a Polyacid–Epoxy Condensation Reaction

J. Fellers

Ford Motor Company, Scientific Research Staff, Dearborn, Michigan 48121.

Received May 16, 1969

ABSTRACT: The kinetics of a tertiary amine catalyzed condensation of a diepoxide with a polymeric carboxyl acid were studied in bulk by infrared spectroscopy and in solution by gel point determination. The rate in the bulk reaction is given by rate α[epoxy][COOH]$^{1/4}$[R$_3$N]$^{1/4}$. and in solution by rate α[epoxy][COOH)$^{1/2}$[R$_3$N]$^{1/2}$. The difference in mechanism between the bulk and the solution reaction is due to an apparent difference in association of the carboxylamine salt in bulk *vs.* solution. A detailed mechanism and kinetic experiments for both cases are presented.

The kinetics, mechanism, and the chemistry of several epoxy reactions have been reported;[1–5] these include the primary, secondary, and tertiary amine activated polymerization of epoxies; epoxy–acid anhydride, and epoxy–hydroxyl reactions. Limited attention has been given to the tertiary amine catalyzed carboxy–epoxy reaction in cross-linking systems;[3] no published information exists on quantitative kinetic parameters for this reaction.

The generally accepted features of this reaction are as follows.[2,3] (a) Carboxyl and amine interact to produce the carboxylate anion which attacks the oxirane ring. Phenolate and aliphatic alkoxide ions also attack the oxirane ring and the order of reactivity toward this group is carboxyl > phenol > aliphatic alcohol. (b) The overall carboxyl–epoxy reaction depicted schematically is selective—other possible reactions do not occur until all carboxyl is consumed.

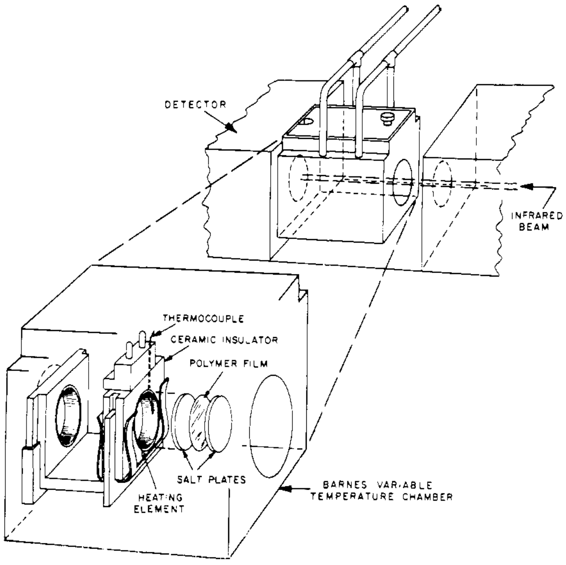
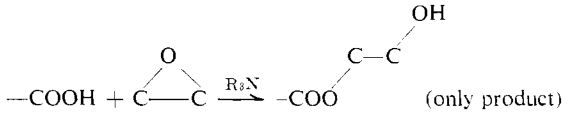


Figure 1. Schematic diagram of the modified Barnes variable-temperature chamber for the infrared measurements.



The nature of the interaction of carboxyl and tertiary amine to produce a carboxylate anion or precursor is not understood.

Investigation of the overall reaction was undertaken to provide more details about the above interaction, establish the reaction orders for all reactants, and develop a general rate law for the reaction.

Experimental Section

The kinetic treatment was based on chemical group analysis by infrared spectroscopy for the bulk phase reaction, and gel point determinations for the solution phase reaction.

A. Materials and Procedures for the Ir Study. The acid used in the reaction was a solution polymerized vinyl addition copolymer containing methyl methacrylate and acrylic acid. The acid value of the copolymer was determined by titration (1 equiv of COOH/346 g).

A commercial diepoxide, Epon 828 (the diglycidyl ether of bis phenol A from Shell Chemical Co.) was used as the crosslinking agent. Titration indicated an epoxide equivalent of 1 equiv/190 g. Tertiary amine catalysts were used as supplied (see Table V).

To prepare films, the diepoxide and acid were weighed and dissolved in acetone; catalyst was added to this solution by pipeting a dilute acetone solution of the amine. The acetone mixtures were cast on Mylar sheet and dried. Resulting films were stored in a desiccator.

Rate studies of the crosslinking reaction were accomplished by following the infrared spectrum of the films heated between salt plates in a specially designed chamber (Figure 1). The temperature of the plates was monitored with a chromel–constantan thermocouple and controlled to ±1°. A Perkin-Elmer Model 521 grating infrared spectrophotometer was used.

B. Procedure for Gel Time Studies. The acid-containing polymer, Epon 828, and tertiary amine were weighed into a ground glass tube fitted with a Teflon stopper, and the appropriate amount of dioxane added to prepare a solution of the desired concentration. These tubes were then placed in a constant-temperature bath controlled to ±1° and the time required for the sample to gel analyzed by monitoring the shear viscosity (Figure 2).

C. Analysis of Ir Data. A typical spectrum of reactants and product at different times is shown in Figure 3. The peak at 2.85 μ is due to -OH (alkyl hydroxy) absorbance of the reaction product. The peak at 3.05 μ is due to -OH absorbance of the -C(=O)OH group. These bands are

---

(1) H. Lee and K. Neville, Encyclopedia of Polymer Science and Technology, Interscience Publishers, New York, N. Y., 1967, pp 209–271.

(2) H. Lee and K. Neville, Handbook of Epoxy Resins, McGraw-Hill Book Co., Inc., New York, N. Y., 1967, pp 5-1–40.

(3) L. Schechtra and J. Wynstra, *Ind. Eng. Chem.*, **48**, 86 (1956).

(4) J. Feltzin, M. K. Barsh, E. J. Peer, and I. Pekter, ACS Symposium, Chicago, Sept 1964, pp 282–289.

(5) I. Smith, *Polymer*, **2**, 95 (1961).

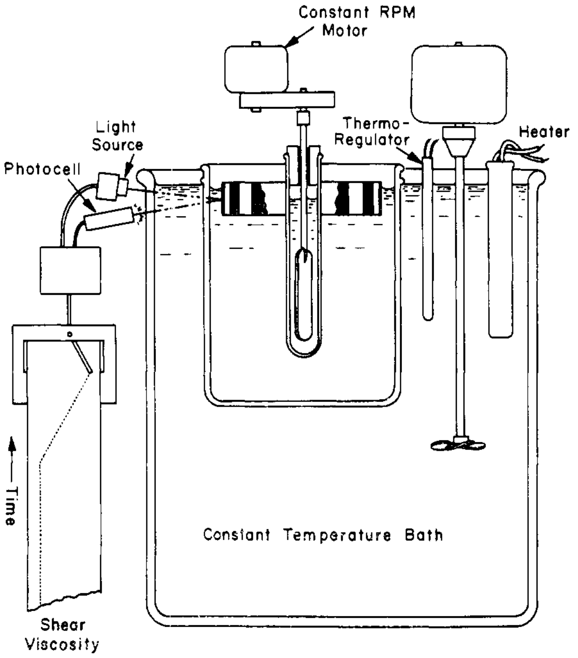


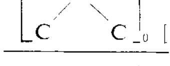
Figure 2. Schematic view of experimental arrangement for gel time measurements.

adjacent and overlap; they also reveal an isoabsorptive point. The significance of this will be discussed later. Quantitative measurements were made using an internal standard, *viz.*, the aromatic ring of Epon 828 and its associated absorption at 6.25 μ. The base-line method was used to measure absorbances; and, the absorptivity ratios, obtained from the internal standard procedure,[6] were used to resolve overlapping peaks by employing the matrix method of analysis[7,8] to convert absorbance ratios into concentrations. The absorptivity ratios used were valid over the first 50% conversion and therefore all infrared rate data apply only in this range.

Results

A. Bulk Reaction. At 120°, the change in COOH concentration with time was measured in triplicate when the initial concentration of [oxirane]/[carboxyl] was 4, 3, 2, and 1, at a fixed concentration of dimethylbenzylamine catalyst (Table I and Figure 4).

TABLE I
FIRST-ORDER RATE DEPENDENCE ON EPOXY CONCENTRATION AT 120°
([DIMETHYLBENZYLAMINE] = 7 × 10⁻³ MOL/KG)

 $_0$ $[\mathrm{COOH}]_0$	k_{obsd},[a] % convn/min
4	4.8
3	3.9
2	2.4
1	1.4

[a] k_{obsd} is taken from the carboxyl per cent conversion *vs.* time plot in the 40% conversion range and is the average of two to four runs.

The change of COOH concentration and -OH (product) with time was also measured at 120°, in triplicate at each of four amine (Quinoline) concentrations over a 1000-fold range (Tables II and III). Similar observations were made in triplicate at one amine (Quinoline) concentration at 140°.

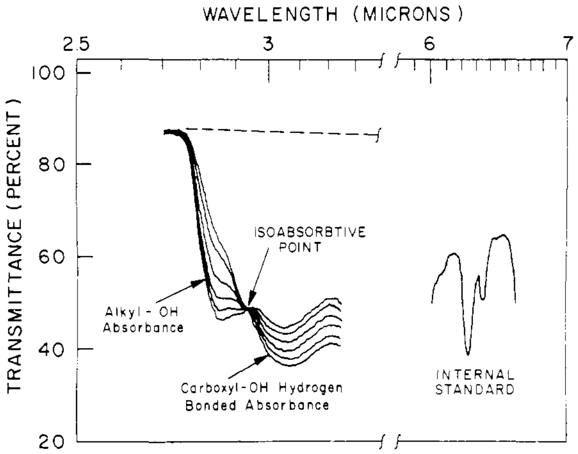
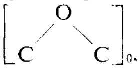


Figure 3. Infrared spectrum depicting the principle features used for this study.

TABLE II
TYPICAL RESULTS FOR THE DISAPPEARANCE OF CARBOXYL FUNCTIONALITY BY INFRARED FOR THE BULK REACTION AT 140°
(QUINOLINE = 3.75 × 10⁻⁶ MOL/KG)

Time, min	COOH, mol/kg	$4/[\mathrm{COOH}]^{1/4}$, $(\mathrm{mol/kg})^{-1/4}$	k, $(\mathrm{kg/mol})^{1/4}$, min^{-1}
0	1.69	3.51	18.0
5	1.53	3.60	20.0
10	1.37	3.70	22.0
15	1.23	3.81	22.0
20	1.11	3.92	16.0
25	1.02	4.00	16.0
30	0.94	4.08	18.0
35	0.85	4.17	

TABLE III
RESULTS OF THE BULK REACTION AT TWO TEMPERATURES AND FOUR CATALYST LEVELS

Temp. °C	$[\mathrm{COOH}]_0$ =  $_0$, mol/kg	Quinoline, mol/kg	Av rate constant, k,[a–c] $(\mathrm{kg/mol})^{1/4}$ min^{-1}
120	1.87	3.75×10^{-3}	$16.1 \times 10^{-3} \pm 1.2$
120	1.87	3.75×10^{-4}	$9.1 \times 10^{-3} \pm 0.8$
120	1.87	3.75×10^{-5}	$4.8 \times 10^{-3} \pm 0.4$
120	1.87	3.75×10^{-6}	$3.2 \times 10^{-3} \pm 0.1$
140	1.87	3.75×10^{-6}	$17.2 \times 10^{-3} \pm 2.5$

[a] All measurements in triplicate. [b] See Figure 5 for a plot of log k *vs.* log $(\mathrm{R_3N})$ which exhibits a slope of 1/4. [c] This k is related to derived constants (eq 7) as $k = k_5[k_4/k_{-4}]^{1/2} \times [k_3/k_{-3}]^{1/4}[\mathrm{R_3N}]^{1/4}$.

All infrared spectra show an isoabsorbtive point which occurs between the OH absorbance of the carboxyl group (reactant) and the OH absorbance of the aliphatic alcohol (product). This feature,[8] along with the concentration calculations from the matrix method

---

(6) A. S. Wexler, *Appl. Spectrosc.*, **19** (No. 4), 135 (1965).
(7) "Progress in Infrared Spectroscopy," H. Szymanski, Ed., Plenum Press, New York, N. Y., 1962, pp 151–166.
(8) "Analytical Absorption Spectroscopy," M. G. Mellon, Ed., John Wiley & Sons, Inc., New York, N. Y., 1950, pp 318.

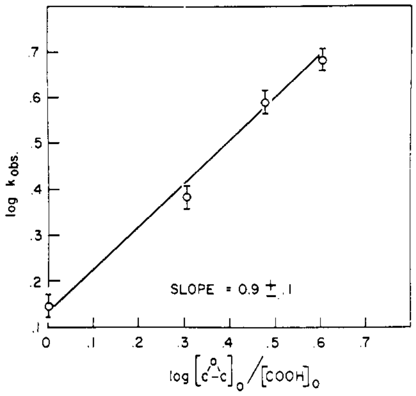
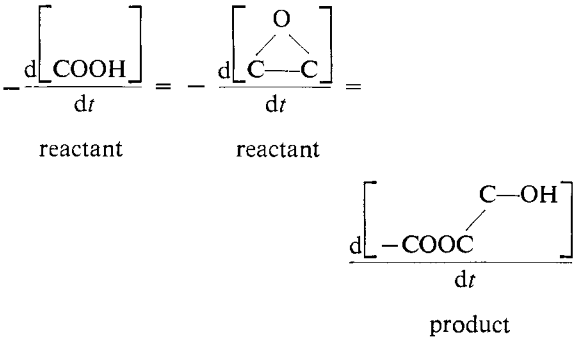


Figure 4. Plot of data in Table I showing first-order dependence on epoxy concentration.

of analysis, is interpreted as evidence for an exclusive reaction between carboxyl and epoxy leading to one product. Furthermore, it may be stated that



$$-\frac{d\left[\mathrm{COOH}\right]}{dt}_{\text{reactant}} = -\frac{d\left[\overset{\mathrm{O}}{\mathrm{C{-}C}}\right]}{dt}_{\text{reactant}} = \frac{d\left[-\mathrm{COOC}\diagup\mathrm{C{-}OH}\right]}{dt}_{\text{product}}$$

This is clearly the case since the concentration of carboxyl groups plus the hydroxyl groups adds to a constant value.

It was found that the data best fit a first-order plot for epoxy (Table I and Figure 4) and a five-fourths-order plot for the product of the epoxy and carboxyl concentrations (Table II and Figure 5). From a log–log plot of the calculated rate constant, k, at 120° *vs.* amine concentration, it was established that $k \propto [\mathrm{R_3N}]^{1/4}$. These results are shown in Table III and Figure 6.

Employing k values at 120 and 140°, the activation energy, E_A, for the bulk reaction was found to be 27 ± 2 kcal/mol with quinoline as catalyst.

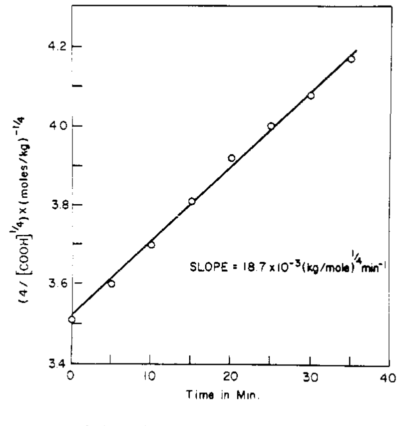


Figure 5. Plot of data in Table II in accordance with eq 13 for the bulk reaction. Slope equals k.

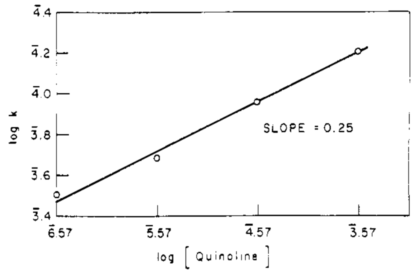


Figure 6. Log–log plot of calculated rate constant, k (Table III) *vs.* quinoline concentration showing fourth-order dependence.

B. Solution Reaction. To establish the influence of catalyst on the cross-linking reaction in solution, gel times at two amine concentrations were determined.

Since the gel point represents a fixed conversion when the epoxy and polyacid concentrations are held constant, the gel times provide a relative measure of overall reaction rate. From gel times (Table IV), the reaction rate was found to be proportional to $[\mathrm{R_3N}]^{1/2}$ in solution.

Table IV
Gel Time as a Function of Quinoline Concentration in Solution at 60°, in Dioxane

[Quinoline], mol/kg	Gel time, hr	Reaction order
0.14	31	½
0.14	32	
1.4	11	
1.4	11	

Activation energies (Table V) were also determined from gel times at several different temperatures. E_A values are seen to differ in solution from bulk; see Discussion.

Table V
Effect of Amine Structure on Activation Energy

Tertiary amine catalyst	E_A,[a] kcal/mol	Reaction order[b]
Dimethylbenzylamine	10 ± 1	
Pyridine	15 ± 1	
2-Picoline	13 ± 1	
Quinoline	16 ± 1	½

[a] From measurements at 30 and 60° for the first three catalysts and at 40, 50, and 70° for quinoline. [b] Note half dependence for quinoline compared to fourth dependence in bulk.

Discussion

A. Kinetic Treatment for the Bulk Reaction. The previous observations can be rationalized in terms of the following kinetic scheme.

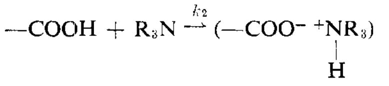
It is well established that carboxylic acid groups are dimerized by hydrogen bonding and that the dimer and monomer are in equilibrium[9]

---

[9] G. Pimental and A. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 366.

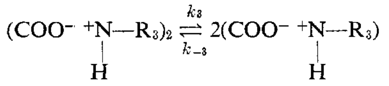
$$(\mathrm{COOH})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2(\mathrm{COOH}) \qquad (1)$$

In this study the initial ratio of carboxylic acid to amine is 500 or greater. Thus, the carboxylic acid and amine react to form the ion pair

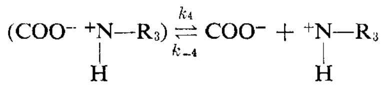

$$\text{—COOH} + \mathrm{R_3N} \xrightarrow{k_2} (\text{—COO}^- \ {}^{+}\underset{\mathrm{H}}{\mathrm{N}}\mathrm{R_3})$$

(2)

Conductivity and freezing point depression measurements have definitely established that in low dielectric strength media, ion pairs associate to form quadrupole ions.[10] Thus the following set of equilibria exist, with the position of the equilibria far to the left

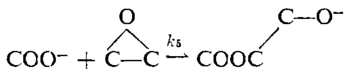

$$(\mathrm{COO^-}\ {}^{+}\underset{\mathrm{H}}{\mathrm{N}}\text{—}\mathrm{R_3})_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} 2(\mathrm{COO^-}\ {}^{+}\underset{\mathrm{H}}{\mathrm{N}}\text{—}\mathrm{R_3})$$

(3)


$$(\mathrm{COO^-}\ {}^{+}\underset{\mathrm{H}}{\mathrm{N}}\text{—}\mathrm{R_3}) \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{COO^-} + {}^{+}\underset{\mathrm{H}}{\mathrm{N}}\text{—}\mathrm{R_3}$$

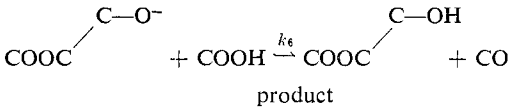
(4)

The reaction then proceeds through the attack of the carboxylate anion on the oxirane ring. This is a generally accepted feature for the overall reaction[3]



(5)

The alkoxide anion thus formed is a stronger base than the carboxylate anion and therefore will react with the proton donor present (carboxyl group), to regenerate carboxylate anion



(6)

This mechanism then explains the observed features of this reaction in the bulk and the following rate law is derived on the basis of the above steps

$$\text{rate} = k_5\left[\overset{\mathrm{O}}{\mathrm{C{-}C}}\right]\left[\frac{k_4}{k_{-4}}\right]^{1/2}\left[\frac{k_3(\mathrm{COO^-\,{}^{+}NH{-}R_3})_2}{k_{-3}}\right]^{1/4} \qquad (7)$$

To obtain a more useful form of this rate expression, it must be integrated. This is readily accomplished if one keeps in mind (a) the $\mathrm{R_3N}$ concentration is not time dependent, and (b) at any time during the reaction, the number of carboxyl groups equals the number of oxirane groups. This is demonstrated by the isoabsorptive point and the matrix method of analysis concentration calculations.

Let X = [epoxy] = [COOH], then substitute into eq 7

$$-\frac{\mathrm{d}X}{\mathrm{d}t} = k_5\left[\frac{k_4}{k_{-4}}\right]^{1/2}\left[\frac{k_3}{k_{-3}}\right]^{1/4}[\mathrm{R_3N}]^{1/4}X^{5/4} \qquad (8)$$

which integrates from t_0 to t and X_0 to X to yield

$$\frac{4}{X^{1/4}} - \frac{4}{X_0^{1/4}} = k_5\left[\frac{k_4}{k_{-4}}\right]^{1/2}\left[\frac{k_3}{k_{-3}}\right]^{1/4}[\mathrm{R_3N}]^{1/4}t \qquad (9)$$

Equation 9, the integrated form of the rate expression, can be used to demonstrate the agreement between the experimental data and the postulated mechanism for the bulk reaction as shown in Tables II and III and Figures 5 and 6.

B. Consideration of the Solution Reaction. The kinetic data in the present study argue against quadrupole ion formation in dioxane. The kinetics of this reaction in dioxane point to ion pair formation, but not quadrupole ions. Unfortunately no direct evidence on the state of association for carboxyl amine salts in dioxane is available. However, some infrared evidence for the solvating ability of dioxane[11] supports the formation of ion pairs and reduced quadrupole ion formation by dioxane solvation of the ion pair. If the equilibrium position of step 3 is shifted to the right because solvation would inhibit quadrupole ion formation, then only solvated ion pairs have a kinetic effect, and one may rationalize the data for the solution reaction.

On the basis of a dioxane solvated ion pair, one may state the following derived rate expression

$$\text{rate} = k_5\left[\overset{\mathrm{O}}{\mathrm{C{-}C}}\right]\frac{\left[k_4(\mathrm{COO^-}\ {}^{+}\underset{\mathrm{H}}{\mathrm{N}}\text{—}\mathrm{R_3})\right]^{1/2}}{k_{-4}} \qquad (10)$$

Equation 10, in differential form, is suitable for demonstrating the correspondence between the half-order dependence on amine that was experimentally observed and the half-order predicted by this mechanism.

The difference between the dioxane solution reaction and the bulk reaction, *i.e.*, half- *vs.* fourth-order dependence on amine concentration, can be explained by ion association. The solvating ability of dioxane breaks up quadrupole ion formation enough so that they exhibit no kinetic effect. Ion association also explains the difference in activation energies, 16/kcal/mol *vs.* 27 kcal/mol for solution *vs.* bulk, respectively. The formation of the carboxylate anion is a higher energy step in bulk due to higher association.

Summary

The kinetics and reaction path of the condensation of a diepoxide and polymeric carboxyl acid has been investigated in solution and in the bulk at elevated temperatures. Infrared spectroscopy and gel point determinations were used to follow the reaction.

In the bulk reaction, the ir spectrum shows an isoabsorptive point which indicates that the reaction follows one path exclusively and that no by-products are formed. Analysis of the spectra by the matrix method substantiates the latter conclusion and was used to determine the carboxyl concentrations as a function of time. The overall rate may be stated as $-\mathrm{d[COOH]}/\mathrm{d}t \propto [\text{epoxy}][\mathrm{COOH}]^{1/4}[\mathrm{R_3N}]^{1/4}$.

Gel point determinations in solution demonstrate

---

[10] H. S. Harned and B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, p 302–303; R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, **55**, 3614 (1933); W. F. Luder and C. A. Kraus, *ibid.*, **58**, 255 (1936); R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 21 (1933); F. M. Batson and C. A. Kraus, *ibid.*, **56**, 2017 (1934); C. A. Kraus and R. A. Vingee, *ibid.*, **56**, 511 (1934); F. M. Batson and C. A. Kraus, *ibid.*, **56**, 2017 (1934).

[11] L. J. Bellamy, "Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p 166; M. Flett, *J. Chem. Soc.*, 962 (1951); G. Fraenkel, R. L. Belford, and P. G. Yankwich, *J. Amer. Chem. Soc.*, **76**, 15 (1954)

that the reaction order of the amine is half *vs.* fourth for the bulk reaction. This difference is ascribed to some change in the state of association of ion pairs in dioxane. The activation energy for the reaction decreases from bulk to solution due to the difference in the state of ion pair association. The overall rate may be stated as $-d[COOH]/dt \propto [epoxy][COOH]^{1/2}[R_3N]^{1/2}$. Both the inherent rate and the thermal sensitivity of the reaction rate are affected by the structure of the catalyst.

Discussion of the kinetics of this reaction is based on associated and solvated ion pairs. A coherent mechanism is proposed for the reaction in bulk and solution, and rate laws derived for both cases.

Acknowledgments. The author expresses his appreciation to Messrs. John Parsons and Ernest Scharhag for their help in developing the infrared technique, and to Drs. Seymour Newman and Lee Mahoney for many helpful discussions and suggestions during the course of this work.

Physicochemical Studies of Polyhexene-1. Polymerization Kinetics

C. F. Tu, J. A. Biesenberger, and S. S. Stivala

Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030. *Received October 20, 1969*

ABSTRACT: A kinetic study of hexene-1 polymerization in cyclohexane solvent with the catalyst system α-$TiCl_3$–$AlEt_2Cl$ was conducted. Correlations in terms of monomer, catalyst and cocatalyst concentrations were proposed for rate of polymerization R_p and average degree of polymerization $\bar{X}_n$, and activation energies of 10.6 and −18.5 kcal/mol, respectively, for these reaction variables were measured. Stationary rates of polymerization and molecular weights were observed and it was concluded that monomer and $TiCl_3$ were involved in chain-breaking processes.

Many kinetic studies of polymerizations catalyzed with Ziegler–Natta-type catalysts have been reported in the literature. Most of these studies involved ethylene and propylene, probably because of their industrial importance, although other monomers such as styrene, butene-1, isoprene, and 4-methylpentene-1 have also been investigated. The most popular catalyst systems studied consisted of $TiCl_4$ or $TiCl_3$ as the catalyst and $AlEt_3$ or $AlEt_2Cl$ as the cocatalyst although $Al(i\text{-}Bu)_3$ has also been used as a cocatalyst.

Most polymers prepared with Ziegler–Natta catalysts are crystalline and, therefore, have poor solubility characteristics. As a consequence they often precipitate out of solution during polymerization and trap the heterogeneous catalyst in a polymer matrix. This impairs kinetic measurements and has caused some workers to consider the possibility that diffusion of monomer to the polymerization sites might interfere with or even control the observed rates of polymerization and others[1] to go to high polymerization temperatures in order to maintain the polymers in solution. Moreover, it is very difficult to analyze accurately the solution properties of these polymers, which should yield valuable information about such important kinetic variables as average molecular weight and molecular weight distribution.

For these reasons we have chosen hexene-1 as our monomer. Hexene-1 is a liquid and it may be polymerized readily with Ziegler–Natta catalysts to a high molecular weight, rubbery polymer which is soluble in most common organic solvents at room temperature. An investigation of the polymerization of hexene-1 to liquid polymer with the catalyst system $TiCl_4$–$AlEt_3$ has previously been reported.[2]

Kinetic studies of α-olefin polymerization with Ziegler–Natta catalysts are also affected by the type, composition, and, sometimes, the method of preparation of the catalyst system. The use of $TiCl_4$ is accompanied by a complex reduction reaction in which titanium is reduced to lower valence states whereas the choice of the system α-$TiCl_3$–$AlEt_3$ avoids this complication and often leads to more stereospecific polymers *via* stationary-state rates of polymerizations.[3] Using $AlEt_2Cl$ as cocatalyst instead of $AlEt_3$ may result in still higher stereospecificity but with polymerization rates which are concomitantly lower and which sometimes do not achieve a stationary state.[4] High rates can be maintained by using Al-reduced $TiCl_3$.

In the present study we have used the catalyst system Al-reduced α-$TiCl_3$ and $AlEt_2Cl$ because we found that $AlEt_3$ and $Al(i\text{-}Bu)_3$ cocatalysts gave us polymerization rates which were too rapid to be measured accurately at low conversions.

Another problem commonly encountered with Ziegler–Natta polymerizations is the difficulty in obtaining reproducible kinetic data owing to the extreme sensitivity of the catalyst components to their environment during catalyst preparation. In order to eliminate this problem all catalysts were prepared under an inert atmosphere in a high-vacuum glove box.

---

(1) D. F. Hoeg and S. Liebman, *Ind. Eng. Chem., Process Des. Develop.*, **1**, 120 (1962).

(2) E. J. Badin, *J. Amer. Chem. Soc.*, **80**, 6549 (1959).

(3) G. Natta and I. Pasquon, "Advances in Catalysis," Vol. 11, Academic Press, New York, N. Y., 1959.

(4) A. D. Caunt, *J. Polym. Sci., Part C*, **4**, 49 (1958).