

The Kinetics of Polyesterification. I. Adipic Acid and Ethylene Glycol

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Synopsis

The polyesterification between adipic acid and ethylene glycol in nonequimolar ratios was investigated. The kinetic equations obtained were quite different from those obtained by Flory in equimolar systems. The kinetic equations obtained in this study were $-d[\text{COOH}]/dt = k[\text{COOH}][\text{OH}]^2$ for uncatalyzed polyesterification and $-d[\text{COOH}]/dt = k[\text{COOH}]^2$ for catalyzed polyesterification. The mechanism of the polyesterification of a dibasic acid and a glycol can only be explained by the dissociation effect of hydrogen ion from dibasic acid in glycol.

INTRODUCTION

Many experimental studies on the polyesterification between dibasic acids and glycols have been reported by various authors. Recent textbooks^{1,2} dealing with polymer chemistry treat polyesterification as a simple third-order, irreversible reaction as originally proposed by Flory.³ As Goldschmidt⁴ has shown, the esterification reactions are generally hydrogen ion catalyzed. Therefore, the following rate equation is considered for polyesterification:

$$-d[\text{COOH}]/dt = k[\text{COOH}][\text{OH}][\text{H}^+] \quad (1)$$

According to Flory, polyesterification in the absence of a foreign acid, owing to the catalytic effect of the dibasic acid molecule, is a third-order reaction. The rate of the polyesterification reaction should be written as

$$-d[\text{COOH}]/dt = k[\text{COOH}]^2[\text{OH}] \quad (2)$$

On the other hand, in the presence of foreign acid, the hydrogen ion derives mainly from the added acid. The polyesterification is thus a second-order reaction:

$$\begin{aligned} -d[\text{COOH}]/dt &= k[\text{COOH}][\text{OH}][\text{H}^+] \\ &= k'[\text{COOH}][\text{OH}] \end{aligned} \quad (3)$$

where the rate constant k' includes the catalyst concentration. During the past 20 years, several investigators have published data which appear to show that Flory's assumption is invalid.

Tang and Yao⁵ have examined nonequimolar ratio systems and proposed a new kinetic equation. Campbell et al.⁶ have shown that the rate of esterification

can be affected by film thickness and water content of the atmosphere. Thus, the view by earlier workers that the polyesterification corresponds to a continuous increase in kinetic order, becoming approximately third order at the later stage of reaction in the absence of catalyst or that it is a simple second order in the presence of catalyst or that the order of reaction is more complicated in the nonequimolar ratio, are all refuted, and the long-disputed question of the order of the polyesterification is clarified in this work.

EXPERIMENTAL

Materials. Adipic acid of reagent grade was recrystallized from conductivity water; mp 151.5°C. Ethylene glycol was obtained by distillation of a chemical grade. As catalyst, *p*-toluenesulfonic acid of reagent grade was used with no further purification.

Apparatus. The apparatus consisted of a Pyrex bulb of about 100-cc capacity sealed to the bottom of a 2.5-cm-diameter tube about 20-cm long. Through a stopper at the top of this tube, a pipet was inserted. The pipet was used to remove samples, and also for admitting a slow stream of nitrogen through the reaction mixture in order to facilitate removal of water formed. The effluent stream of nitrogen and water vapor passed through a long reflux condenser, by which the loss of glycol was minimized. The stream was then led downward from a side tube at the top of condenser, where the temperature was kept at about 110°C, to a cooling graduated bottle to collect water.

Procedure. The mixture of glycol, to which the *p*-toluenesulfonic acid was added in the case of acid-catalyzed reaction, and adipic acid in nonequimolar ratio was placed in the reaction bulb. The reactants should be preheated before they are placed together in the reaction bulb. Nitrogen was bubbled through the mixture, which was quickly raised to reaction temperature. The reaction mixture can be withdrawn, weighed, dissolved with mixed solvent (benzene, isopropanol, and methanol in equivolume), and titrated with methanolic KOH, using phenolphthalein as indicator. A sharp endpoint was always observed. If the concentration change due to the removal of water is taken into consideration, the acid concentration may be calculated according to the following equation:

$$C = \frac{C_e(W_0 - 18) \times 1000}{W_0(1000 - 18C_e)} \quad (4)$$

where C is the actual acid concentration, in equivalent moles per kg sample, including water produced; C_e is the apparent acid concentration, in equivalent moles per kg sample; and W_0 is the total mass of reaction mixture based on one equivalent mole of adipic acid. The degree of polymerization can be calculated by the following equation.

$$\text{D.P.} = \frac{1 + r}{1 + r - 2P} \quad (5)$$

where r represents the initial molar ratio between [OH] and [COOH] and is always set to be more than unity in this investigation.

THEORETICAL CONSIDERATIONS

It has been suggested in the past that the esterification reactions are hydrogen ion catalyzed. The rate of polyesterification as expressed in eq. (2) for an uncatalyzed reaction in nonequimolar ratio can be written as

$$-dC/dt = kC^2(C + a) \quad (6)$$

where $C = [\text{COOH}]$, $C + a = [\text{OH}]$, and $a = (r - 1)C_0$. Upon integration, we obtain

$$\frac{a}{C} - \ln \frac{C + a}{C} = a^2kt + k_a = k_1t + k_a \quad (7)$$

where $k_a = (a/C_0) - \ln r$ and $k_1 = a^2k$. In terms of $P = (C_0 - C)/C_0$ and $a = (r - 1)C_0$, eq. (7) becomes

$$\frac{r - 1}{1 - P} - \ln \frac{r - P}{1 - P} = k_1t + k_a \quad (8)$$

For an equimolar reaction, i.e., $a = 0$, eq. (6) is simplified to

$$-dC/dt = kC^3 \quad (9)$$

Upon integration, it becomes

$$2kt = \frac{1}{C^2} - \frac{1}{C_0^2} \quad (10)$$

and

$$2C_0^2kt = \frac{1}{(1 - P)^2} - 1 \quad (11)$$

This is the equation obtained by Flory.³ If the polyesterification proceeds by another type of kinetics as shown in the following equation:

$$-d[\text{COOH}]/dt = k[\text{COOH}][\text{OH}]^2 \quad (12)$$

then, analogous to eq. (6), the net rate of reaction would be

$$-dC/dt = kC(C + a)^2 \quad (13)$$

Upon integration, it yields

$$\ln \frac{r - P}{1 - P} - \frac{r - 1}{r - P} = a^2kt + k_b = k_1t + k_b \quad (14)$$

where $k_b = \ln r - (r - 1)/r$ and $k_1 = a^2k$. A plot of $\ln [(r - P)/(1 - P)] - [(r - 1)/(r - P)]$ vs t should be linear.

In the case of acid-catalyzed polyesterification, the rate of reaction according to Flory's concept of eq. (3) will be

$$-dC/dt = k'C(C + a) \quad (15)$$

Such a rate is given by

$$\ln \frac{r - P}{1 - P} = ak't - \ln \frac{1}{r} = k_2t + k_c \quad (16)$$

where $k_c = -\ln(1/r)$ and $k_2 = ak'$. If this acid-catalyzed reaction proceeded by the following kinetic type instead of eq. (3),

$$-d[\text{COOH}]/dt = k''[\text{COOH}]^2 \quad (17)$$

then it is a second-order reaction with respect to $[\text{COOH}]$. This equation integrates to

$$\frac{1}{C} - \frac{1}{C_0} = k''t \quad (18)$$

When $C = C_0(1 - P)$ is substituted, eq. (18) becomes

$$C_0 k'' t = \frac{1}{1 - P} - 1 \quad (19)$$

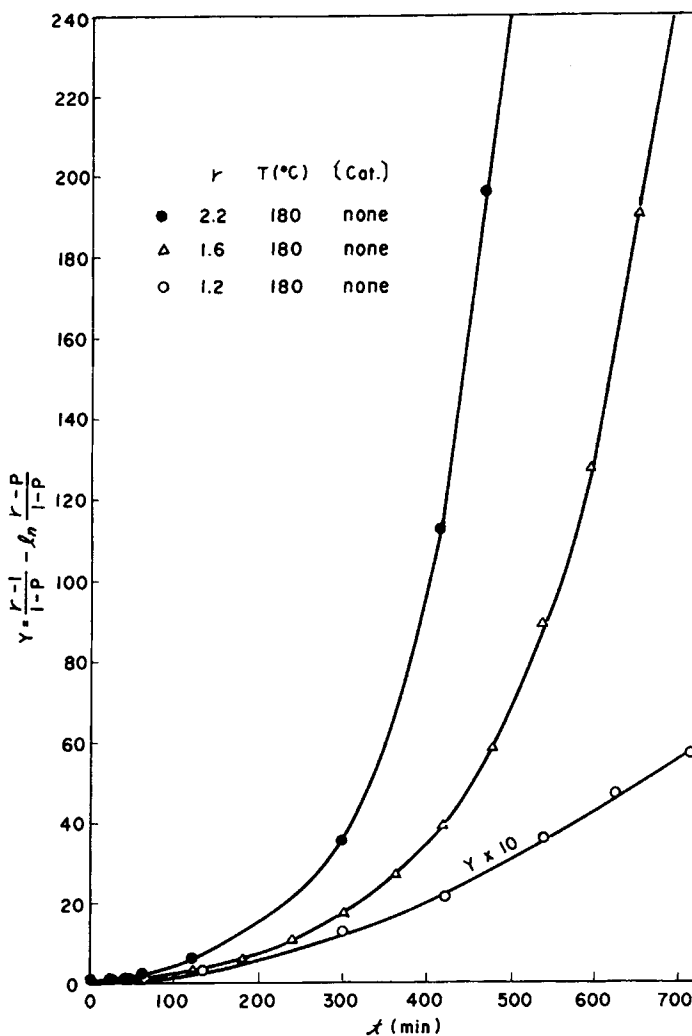


Fig. 1. Uncatylzed polyesterification of nonequimolar quantities of adipic acid and ethylene glycol. Plots of $(r - 1)/(1 - P) - \ln [(r - P)/(1 - P)]$ vs reaction time all give no straight lines.

Flory's kinetics of eq. (3) can coincide fortuitously with the result of eq. (19) only for the system of equimolar reactants.

RESULTS AND DISCUSSION

The typical experimental data of the polyesterification between nonequimolar quantities of adipic acid and ethylene glycol of $r = 1.6$ in the absence of foreign acid at a constant temperature of 180°C are listed in Table I. For brevity, the analytical data of subsequent experiments under various r values are not tabulated.

All the results plotted as indicated by eq. (8) are shown in Figure 1. On the other hand, the results plotted as indicated by eq. (14) are shown in Figure 2. At first glance, the data seem fairly well represented by eq. (14) rather than eq. (8) over the range of $P = 0$ up to $P = 0.99$. Evidently, these are third-order kinetics not according to eq. (2), but eq. (12). The correspondence between theory and data in Flory's experiments³ can be regarded as fortuity of an equimolar reaction, to which eq. (9) is applicable for both kinetic types of eqs. (2) and (12).

The apparent agreement between theory and experiment of Flory has resulted in a misconception. It is interesting to point out that the polyesterification for a larger molar ratio (for instance, $r = 4$) indicates a linear relationship when it is plotted only on the basis of the proposed mechanism as indicated by eq. (17). This means that the reaction is now second order with respect to $[\text{COOH}]$. We

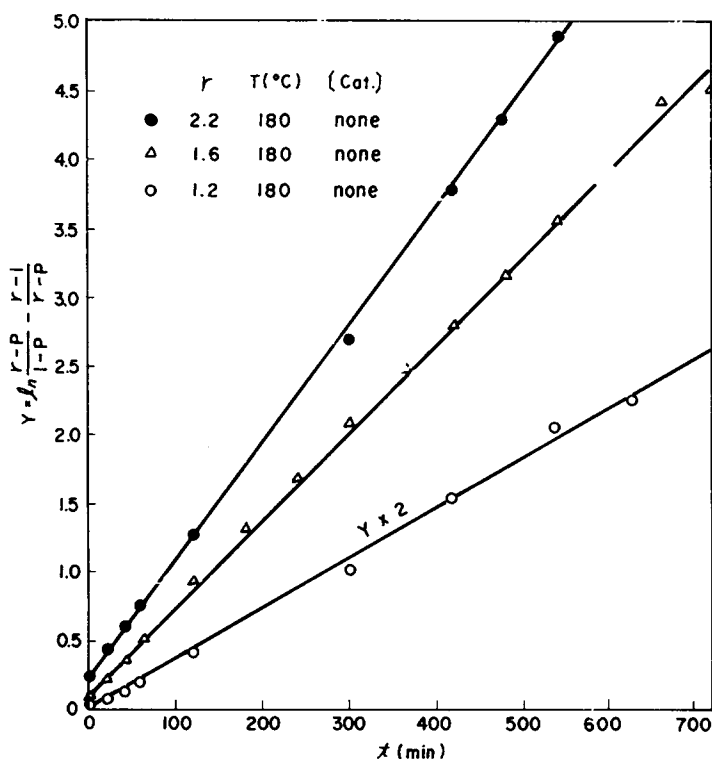


Fig. 2. Uncatalyzed polyesterification of nonequimolar quantities of adipic acid and ethylene glycol. Plots of $\ln [(r - P)/(1 - P)] - (r - 1)/(r - P)$ vs reaction time all give straight lines.

TABLE I
 Adipic Acid-Ethylene Glycol^a

t , min	C , equiv. moles kg sample	P	D.P.	$\frac{r-1}{1-P} - \ln \left(\frac{r-P}{1-P} \right)$	$\ln \left(\frac{r-P}{1-P} \right) - \frac{r-1}{r-P}$
0	8.149	0.000	1.000	0.130	0.095
20	4.490	0.449	1.528	0.352	0.216
40	2.865	0.648	1.994	0.710	0.365
60	2.059	0.747	2.351	1.158	0.512
120	1.108	0.875	3.059	3.045	0.930
180	0.603	0.926	3.476	5.899	1.319
240	0.374	0.954	3.757	10.428	1.715
300	0.244	0.970	3.939	16.991	2.094
365	0.165	0.980	4.063	26.208	2.455
420	0.116	0.986	4.140	38.382	2.788
480	0.078	0.990	4.194	58.525	3.170
540	0.0526	0.994	4.248	88.404	3.554
600	0.0369	0.995	4.262	127.600	3.901
660	0.0250	0.997	4.290	190.279	4.286
720	0.0180	0.998	4.305	266.003	4.512
780	0.00852	0.999	4.319	833.680	5.356

$r = 1.6$, $T = 180^\circ\text{C}$, [Cat.] = none.

believe that hydrogen ion has resulted from the dissociation of acid in combination with the solvent. Ethylene glycol will act as the solvent in this case. Since adipic acid dissociates in ethylene glycol very incompletely only in the magnitude of 0.390 mole/mole ethylene glycol even at 180°C , the concentration of hydrogen ion does not depend on the concentration of adipic acid added, but on the concentration of ethylene glycol presented in the system. Thus,

$$[\text{H}^+] = k_h[\text{OH}] \quad (20)$$

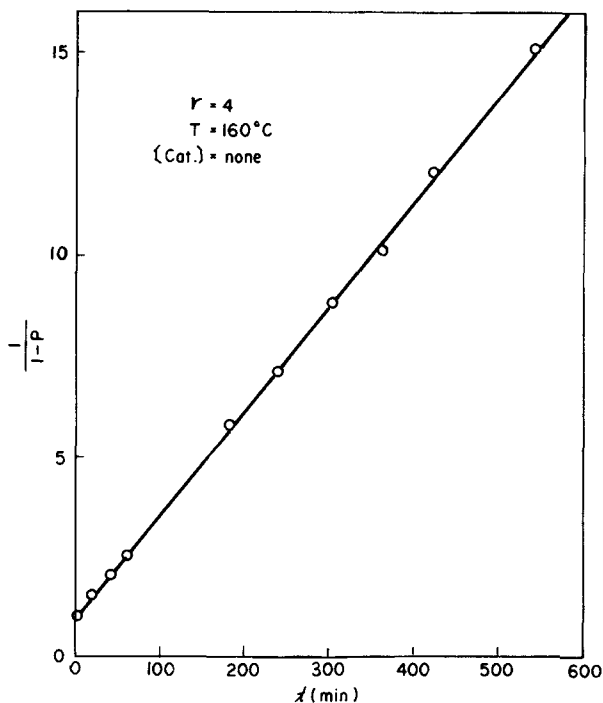


Fig. 3. Uncatalyzed polyesterification of adipic acid and ethylene glycol in large excess of ethylene glycol. Plot of $1/(1-P)$ vs reaction time gives a straight line.

TABLE II
Adipic Acid-Ethylene Glycol^a

t , min	C , equiv. moles kg sample	P	D.P.	$\ln\left(\frac{r-P}{1-P}\right)$	$\frac{1}{1-P}$
0	8.133	0.0000	1.000	0.4700	1.0000
20	1.0478	0.8712	3.032	1.7331	7.7620
40	0.3994	0.9509	3.724	2.5817	20.3630
90	0.2126	0.9739	3.987	3.1776	38.2549
150	0.1232	0.9849	4.126	3.7071	66.0146
180	0.0941	0.9884	4.172	3.9651	86.4293
240	0.0787	0.9903	4.198	4.1408	103.3418
300	0.0624	0.9923	4.225	4.3685	130.3365
360	0.0547	0.9933	4.239	4.5059	148.6837
420	0.0461	0.9943	4.253	4.6659	176.4208
480	0.0393	0.9952	4.265	4.8363	206.9466

^a $r = 1.6$, $T = 151^\circ\text{C}$, $[\text{Cat.}] = 0.0105$ equiv./kg.

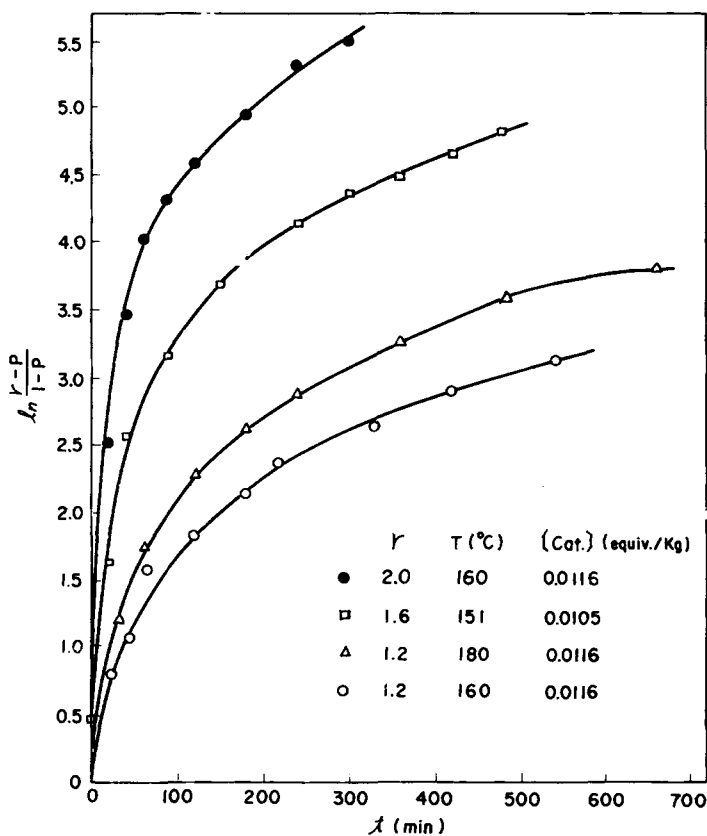


Fig. 4. Catalyzed polyesterification of adipic acid and ethylene glycol. Plots of $\ln[(r-P)/(1-P)]$ vs reaction time all give no straight lines.

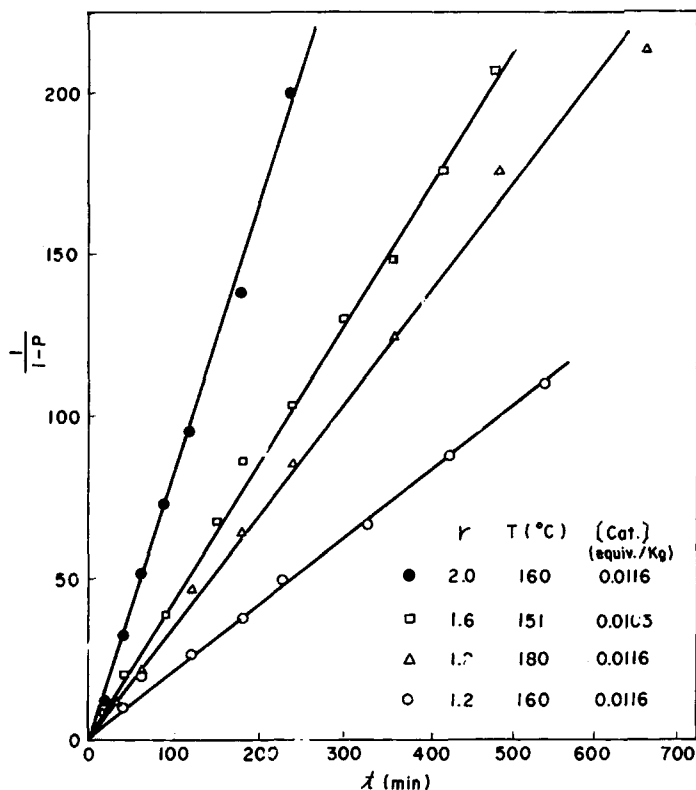


Fig. 5. Catalyzed polyesterification of adipic acid and ethylene glycol. Plots of $1/(1-P)$ vs reaction time all give straight lines.

Substituting eq. (20) into eq. (1), we can obtain eq. (12). In the case of excess of ethylene glycol (generally, $r > 4$), the concentration of hydrogen ion is not saturated and the concentration of hydrogen ion depends on the concentration of acid itself; therefore,

$$[H^+] = k_h'[\text{COOH}] \quad (21)$$

Substituting eq. (21) into eq. (1) and neglecting the concentration change of glycol, we can obtain eq. (17). Figure 3 shows the typical data for an uncatalyzed system in the case of excess in ethylene glycol, which is plotted as indicated by eq. (19).

Several experiments on the reaction of adipic acid with ethylene glycol catalyzed by a small amount of *p*-toluenesulfonic acid (about 0.012 mole per kg mass) were carried out. The typical experimental data of the polyesterification between nonequimolar quantities of adipic acid and ethylene glycol of $r = 1.6$ in the presence of foreign acid at a constant temperature of 151°C are listed in Table II. Figures 4 and 5 show the results plotted as indicated by eq. (16) and eq. (19), respectively. All the results fail to give straight lines with eq. (16) and clearly demonstrate that the reactions do not follow the kinetic type of eq. (3) as proposed by Flory but of eq. (17) proposed by us. The equilibrium expression for the dissociation of an acid in ethylene glycol may be written

$$K_a = \frac{[\text{H}^+][\text{COO}^-]}{[\text{COOH}]} \quad \text{or} \quad [\text{H}^+] = \frac{K_a[\text{COOH}]}{[\text{COO}^-]} \quad (22)$$

where K_a is the apparent acid dissociation constant which is a function of temperature only. In the case of a catalyzed reaction, the concentration of hydrogen ion $[\text{H}^+]$ here is attributed to both added catalyst and adipic acid. This leads to

$$[\text{H}^+] = [\text{H}_h^+] + [\text{H}_a^+]$$

Substituting eq. (22) into eq. (1), we obtain

$$-d[\text{COOH}]/dt = kK_a[\text{COOH}]^2[\text{OH}]/[\text{COO}^-] \quad (23)$$

According to eq. (20), the concentration of hydrogen ion attributed to adipic acid, $[\text{H}_a^+]$, is

$$[\text{H}_a^+] = [\text{COO}^-] = k_h[\text{OH}]$$

The elimination of $[\text{OH}]$, $[\text{COO}^-]$ and $[\text{H}_a^+]$ among these equations leads to

$$-d[\text{COOH}]/dt = k''[\text{COOH}]^2$$

where $k'' = kK_a/k_h$. Our experimental results with the acid-catalyzed system are also in good agreement with eq. (17).

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