

# Kinetics of Polyesterification of 1,3-(Dicarboxymethoxy)benzene with Tetraethylene Glycol

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## Synopsis

The polyesterification of 1,3-(dicarboxymethoxy)benzene with tetraethylene glycol in both equimolar and nonequimolar ratios were studied over the range of 120–160°C in the absence and presence of *p*-toluenesulphonic acid as catalyst. The experimental results for uncatalyzed reactions agreed quite well with the kinetic equation proposed by Flory. The kinetic equations for acid-catalyzed reactions, however, are in agreement with the kinetic equation proposed by Lin and Hsieh. The kinetic equations were  $-d[\text{COOH}]/dt = k_1[\text{COOH}]^2[\text{OH}]$  and  $-d[\text{COOH}]/dt = k_2[\text{COOH}]^2$  for uncatalyzed and acid-catalyzed polyesterifications, respectively. The rate constants for uncatalyzed and acid-catalyzed reactions were calculated by using the method of least squares for various values of initial molar ratio between  $[\text{OH}]$  and  $[\text{COOH}]$ . Also, the activation energies were calculated.

## INTRODUCTION

Polyesterification is a classical example of a step-growth polymerization. Many kinetic studies on the polyesterification reactions between dibasic acids and glycols have been reported by various authors. From these studies, a variety of conclusions have been reached regarding the kinetic order and hence the mechanism of the reaction. Thus the conclusions have been reached that the reaction follows third-order,<sup>1</sup> second-order,<sup>2</sup> second-order followed by a third-order,<sup>2</sup> and two-and-a-half-order kinetics.<sup>3–6</sup> Textbook<sup>7,8</sup> dealing with polymer chemistry treat polyesterification as a simple third-order, irreversible reaction as originally proposed by Flory.<sup>1</sup> He concluded that the kinetic behavior of polyesterification should be

$$-d[\text{COOH}]/dt = k_1[\text{COOH}]^2[\text{OH}] \quad (1)$$

for uncatalyzed reactions and

$$-d[\text{COOH}]/dt = k'_2[\text{COOH}][\text{OH}] \quad (2)$$

for acid-catalyzed reactions, where  $k_1$  and  $k'_2$  are the rate constants.

In our previous work,<sup>9,10</sup> kinetics of polyesterifications of cinnamylsuccinic acid with ethylene and 1,4-tetramethylene glycols were reported. A careful

treatment with nonequimolar reactants between cinnamylsuccinic acid with ethylene or 1,4-tetramethylene glycols has shown that the true kinetic equations of polyesterification are in agreement with those reported by Lin and Hsieh.<sup>11</sup> Accordingly, the kinetic equations obtained were

$$-d[\text{COOH}]/dt = k'_1[\text{COOH}][\text{OH}]^2 \quad (3)$$

for uncatalyzed polyesterification and

$$-d[\text{COOH}]/dt = k_2[\text{COOH}]^2 \quad (4)$$

for acid-catalyzed polyesterification, where  $k'_1$  and  $k_2$  are the apparent rate constants.

In the present work the reaction between 1,3-(dicarboxymethoxy)benzene and tetraethylene glycol is studied by using the kinetic equations proposed by Flory<sup>1</sup> as well as Lin and Hsieh<sup>11</sup> in order to illustrate the true kinetic behavior of polyesterification.

These kinetic parameters are expected to be very useful in selecting suitable hydroxy-terminated polyester resins for the preparation of polyesterurethanes with optimum physical properties;<sup>12</sup> this will be studied in our future work.

### EXPERIMENTAL

1,3-(Dicarboxymethoxy)benzene was prepared by the reaction of monochloroacetic acid with resorcinol according to the method previously described.<sup>13</sup> Tetraethylene glycol was obtained from E. Merck (Darmstadt, Germany) and was used without any further purification. All solvents were of reagent grade and were purified by distillation before use.

Bulk polyesterification of 1,3-(dicarboxymethoxy)benzene with tetraethylene glycol was carried out under a slow stream of dry deoxygenated  $\text{N}_2$ . Kinetic runs were made at 120–160°C using a thermostatically controlled oil bath. The reaction was followed by titration of the total free carboxyl in sample, removed from the reaction mixture at a suitable interval of time according to the method previously described.<sup>9</sup> The extent of the reaction ( $P$ ) was calculated from the equation

$$P = \frac{C'_0 - C'}{C'_0} \quad (5)$$

where  $C'_0$  and  $C'$  are the acid values before the reaction and after time  $t$ , respectively. The degree of polymerization was calculated by using the equation

$$\text{D.P.} = \frac{1 + r}{1 + r - 2p} \quad (6)$$

where  $r$  represents the initial molar ratio between  $[\text{OH}]$  and  $[\text{COOH}]$ , i.e.,  $r = [\text{OH}]_0/[\text{COOH}]_0$ .

## RESULTS AND DISCUSSION

The equimolar and nonequimolar polyesterifications of 1,3-(dicarboxymethoxy)benzene with tetraethylene glycol were studied over the range 120–160°C in the absence and in the presence of *p*-toluenesulphonic acid as catalyst.

**Self-Catalyzed and Acid Catalyzed Polyesterification  
of Equimolar Quantities of 1,3-(Dicarboxymethoxy) Benzene  
and Tetraethylene Glycol at 120–160°C**

The experimental results obtained using equimolar quantities of 1,3-(dicarboxymethoxy)benzene and tetraethylene glycol at 160°C are given in Table I for self-catalyzed reaction. The detailed results for subsequent experiments are not tabulated. For self-catalyzed polyesterifications at various temperatures, the relation between  $1/(1-p)$  and  $1/(1-p)^2$  has been plotted against time, and the quality of fit was tested by using the least square method. The best linear plots were obtained by plotting  $1/(1-p)^2$  vs. time (Fig. 1), indicating that the reaction satisfies the following third-order rate equation

$$2C_0^2 k_1 t = 1/(1-p)^2 - 1 \quad (7)$$

where  $C_0$  is the initial concentration of acid. This equation applies for both kinetic types of eqs. (1) and (3) in equimolar systems.

For acid-catalyzed polyesterifications at various temperatures, the relation between  $1/(1-p)$  and  $1/(1-p)^2$  has been plotted against time, and the goodness of fits was also tested by the least square method. The best linear

TABLE I  
Data on Self-Catalyzed Polyesterification of Equimolar Quantities of  
1,3-(Dicarboxymethoxy)benzene with 1,4-Tetraethylene Glycol<sup>a</sup>

Time (min)	Acid value	<i>P</i>	$1/(1-P)^2$
80	52.48	0.8036	25.90
120	42.98	0.8392	38.61
140	36.79	0.8623	52.63
160	35.11	0.8686	57.80
180	33.44	0.8748	63.69
200	31.65	0.8816	71.43
230	27.77	0.8961	92.59
260	26.89	0.8994	99.01
290	23.47	0.9122	129.87
320	22.44	0.9160	140.85
380	21.32	0.9202	156.25
410	20.40	0.9237	172.41
455	19.35	0.9276	188.68
500	18.93	0.9292	200.00
530	17.39	0.9349	238.10
590	16.70	0.9375	256.41

<sup>a</sup> $C_0 = 2.3799$  mol/kg,  $T = 160^\circ\text{C}$ , [Cat] = 0.

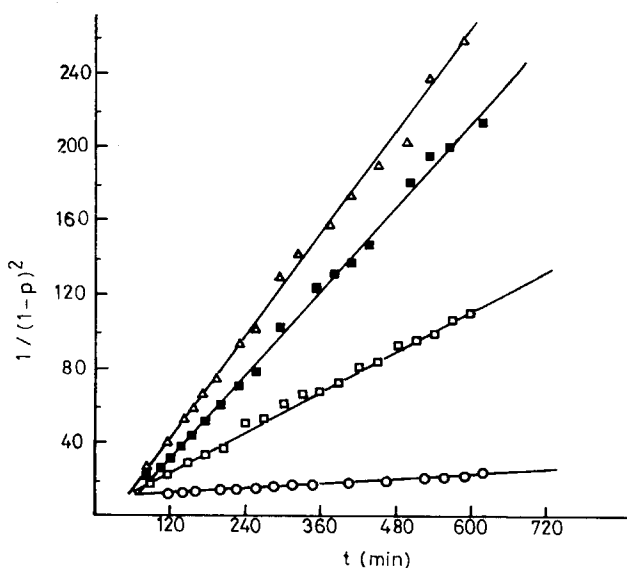


Fig. 1. Plots of  $1/(1-p)^2$  vs. reaction time  $t$ , for equimolar polyesterification reactions of bis-1,3-(Dicarboxymethoxy)benzene with tetraethylene glycol at 120 (○), 140 (□), 150 (■), and 160°C (△) in the absence of catalyst.

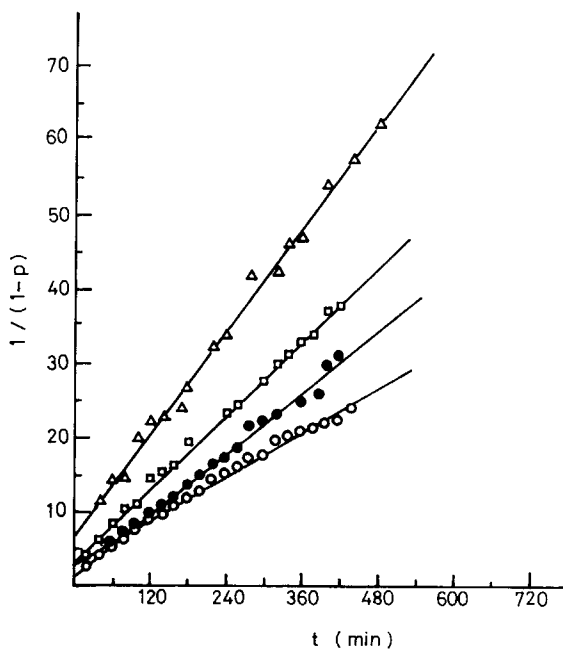


Fig. 2. Plots of  $1/(1-p)$  vs. reaction time  $t$ , for equimolar polyesterification reactions of bis-1,3-(Dicarboxymethoxy)benzene with tetraethylene glycol at 120 (○), 130 (●), 140 (□), and 160°C (△) in the presence of catalyst.

TABLE II  
Rate Constants ( $k_1$  and  $k_2$ ) for Self-Catalyzed and Acid-Catalyzed Polyesterification Reactions of Equimolar Quantities of 1,3-(Dicarboxymethoxy)-benzene and Tetraethylene Glycol<sup>a</sup>

Temperature (°C)	$k_1 \times 10^3$ (kg <sup>2</sup> /mol <sup>2</sup> min)	$k_2 \times 10^3$ (kg/mol min)
120	1.68 ± 0.12	19.97 ± 0.89
130		29.04 ± 0.69
140	16.32 ± 0.45	34.82 ± 0.60
150	33.71 ± 0.69	
160	40.15 ± 0.99	48.51 ± 1.08

<sup>a</sup>[Cat] = 0.0097 mol/kg.

plots were obtained by plotting  $1/(1 - p)$  vs. time (Fig. 2), indicating that the reaction satisfies the second-order rate equation [eq. (8)] which applies for both kinetic types of eqs. (2) and (4) in equimolar systems:

$$C_0 k_2 t = 1/(1 - p) - 1 \quad (8)$$

The rate constants  $k_1$  and  $k_2$  for both the self-catalyzed and acid-catalyzed polyesterification reactions, have been calculated and are presented in Table II. It appears that the rate constants for acid-catalyzed polyesterification are characterized by higher values than those for the uncatalyzed process.

The Arrhenius equation was found to be obeyed since good straight lines were obtained when  $\ln k_1$  and  $\ln k_2$  were plotted vs.  $1/T$  as shown in Figure 3. The activation energies were calculated and were found to be  $117.45 \pm 19.37$  and  $30.29 \pm 3.89$  kJ mol<sup>-1</sup> for self-catalyzed and acid-catalyzed polyesterifications, respectively.

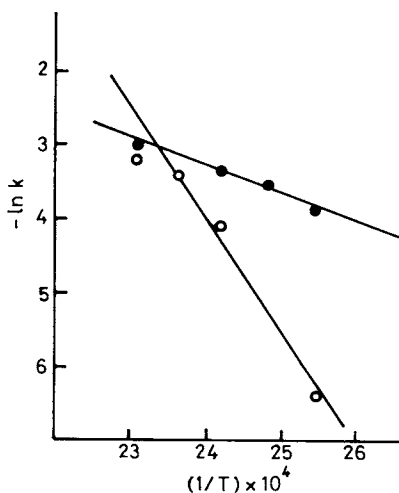


Fig. 3. Plots of  $\ln k_1$  and  $\ln k_2$  vs.  $1/T$  for (○) uncatalyzed and (●) acid-catalyzed polyesterification reactions of bis-1,3-(Dicarboxymethoxy)benzene with tetraethylene glycol in equimolar quantities.

**Self-Catalyzed Polyesterification of Nonequimolar Quantities  
of 1,3-(Dicarboxymethoxy) Benzene and Tetraethylene Glycol  
at 160°C**

Typical experimental data of the polyesterification between nonequimolar quantities of 1,3-(dicarboxymethoxy)benzene and tetraethylene glycol of  $r = 1.6$  for uncatalyzed reaction at 160°C are listed in Table III. Other analytical data of subsequent experiments with various  $r$  values (2.0, 2.5, and 3.0) are not tabulated.

All the results were plotted as indicated by eq. (9) [integrated form of eq. (1)] as shown in Figure 4:

$$\frac{r-1}{1-p} - \ln \frac{r-p}{1-p} = a^2 k_1 t + a/C_0 - \ln r \quad (9)$$

where  $a = (r-1)C_0$ .

Also, the results plotted according to eq. (10) [integrated form of eq. (3)] are shown in Figure 5:

$$\ln \frac{r-p}{1-p} - \frac{r-1}{r-p} = a^2 k_1 t + \ln r - \frac{r-1}{r} \quad (10)$$

At first glance, the data seem fairly well represented by eq. (9) rather than eq. (10). Evidently, these are third-order kinetics according to eq. (1) proposed by Flory.<sup>1</sup> The correspondence between theory (of a dissociation-controlling

TABLE III  
Data on Self-Catalyzed Polyesterification of Nonequimolar Quantities of  
1,3-(Dicarboxymethoxy)benzene with Tetraethylene Glycol<sup>a</sup>

Time (min)	Acid value	$P$	$\frac{r-1}{1-p} - \ln\left(\frac{r-p}{1-p}\right)$	$\ln\left(\frac{r-p}{1-p}\right) - \frac{r-1}{r-p}$
45	65.52	0.6866	0.84	0.41
90	39.38	0.8117	1.75	0.67
135	28.90	0.8618	2.67	0.86
180	23.67	0.8868	3.46	1.00
225	19.81	0.9053	4.34	1.13
270	17.55	0.9161	5.05	1.21
315	15.55	0.9256	5.86	1.31
360	13.47	0.9356	6.98	1.43
405	12.89	0.9384	7.35	1.47
450	11.94	0.9429	8.06	1.53
495	11.54	0.9448	8.40	1.56
540	10.67	0.9489	9.22	1.63
585	9.76	0.9533	10.22	1.70
630	9.09	0.9565	11.10	1.76
675	9.06	0.9567	11.16	1.77
765	8.35	0.9601	12.25	1.83
810	7.95	0.9620	12.96	1.88
900	7.70	0.9632	15.45	1.91

<sup>a</sup>  $r = 1.6$ ,  $C_0 = 1.829$  mol/kg,  $T = 160^\circ\text{C}$ .

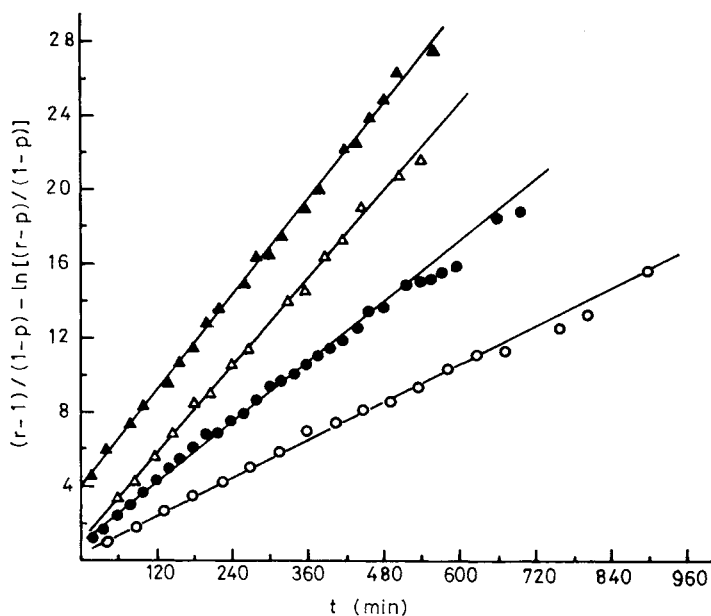


Fig. 4. Plots of  $(r-1)/(1-p) - \ln[(r-p)/(1-p)]$  vs. reaction time  $t$ , for nonequimolar polyesterification reactions of bis-1,3-(dicarboxymethoxy)benzene with tetraethylene glycol at 160°C, in the absence of catalyst.  $r$ : (○) 1.6; (●) 2.0; (△) 2.5; (▲) 3.0.

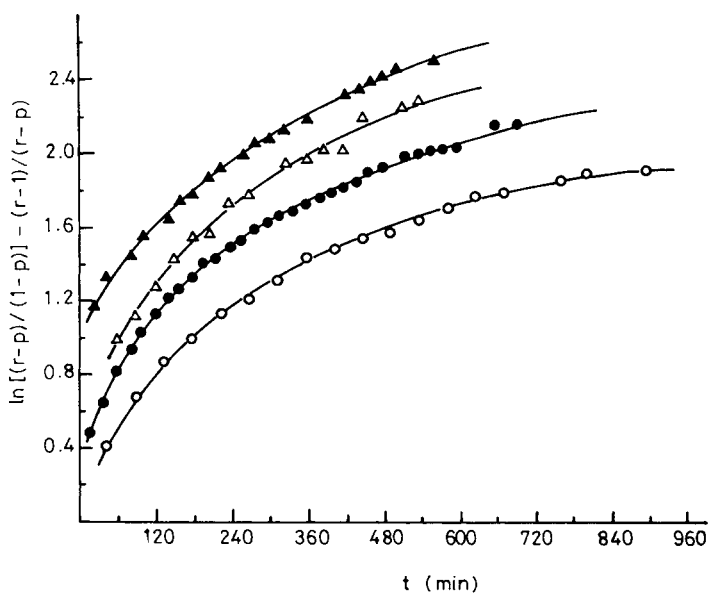


Fig. 5. Plots of  $\ln[(r-p)/(1-p)] - (r-1)/(r-p)$  vs. reaction time  $t$ , for nonequimolar polyesterification reactions of bis-1,3-(dicarboxymethoxy)benzene with tetraethylene glycol at 160°C, in the absence of catalyst.  $r$ : (○) 1.6; (●) 2.0; (△) 2.5; (▲) 3.0.

TABLE IV  
Data on Self-Catalyzed Polyesterification of 1,3-(Dicarboxymethoxy)benzene  
with Excess of Tetraethylene Glycol<sup>a</sup>

Time (min)	Acid value	<i>P</i>	1/(1 - <i>p</i> )
60	28.43	0.5000	2.00
90	21.74	0.6176	2.62
120	18.44	0.6756	3.08
150	17.05	0.7002	3.34
180	14.72	0.7411	3.86
240	12.74	0.7759	4.46
270	12.13	0.7867	4.69
330	10.45	0.8161	5.44
360	9.92	0.8255	5.73

<sup>a</sup>  $r = 9$ ,  $C_0 = 0.5066$  mol/kg,  $T = 160^\circ\text{C}$ .

mechanism proposed by Lin and Hsieh<sup>11</sup>) and Flory's experiments can be regarded as fortuitous for an equimolar reaction, to which eq. (11) is applicable for both kinetic eqs. (1) and (3):

$$-dC/dt = kC^3 \quad (11)$$

The nonequimolar polyesterification of 1,3-(dicarboxymethoxy)benzene with tetraethylene glycol in the absence of catalyst for a large molar ratio ( $r = 9$ ) was studied. The experimental conditions and results are illustrated in Table IV. The results indicate a linear relationship only when plotted on the basis of

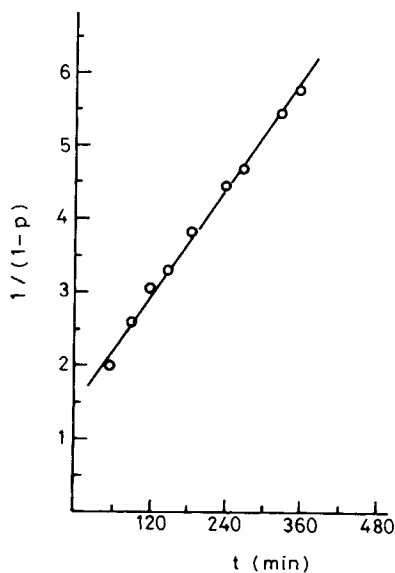


Fig. 6. Plot of  $1/(1 - p)$  vs. reaction time  $t$ , for nonequimolar polyesterification reaction of bis-1,3-(dicarboxymethoxy)benzene with excess of tetraethylene glycol ( $r = 9$ ) at  $160^\circ\text{C}$  in the absence of catalyst.



eq. (12), instead of eq. (1):

$$-d[\text{COOH}]/dt = k_3[\text{COOH}]^2 \quad (12)$$

This means that the reaction is second-order with respect to [COOH]. Figure 6 shows typical data for the uncatalyzed system for excess tetraethylene glycol, plotted according to eq. (13) [integrated form of eq. (12)]

$$C_0 k_3 t = 1/(1 - p) - 1 \quad (13)$$

### Acid-Catalyzed Polyesterification of Nonequimolar Quantities of 1,3-(Dicarboxymethoxy) Benzene and Tetraethylene Glycol at 140°C

Several experiments on the reaction of 1,3-(dicarboxymethoxy)benzene with tetraethylene glycol catalyzed by a small amount of *p*-toluenesulphonic acid at 140°C in nonequimolar ratios ( $r_1 = 1.6, 1.9, \text{ and } 2.2$ ) were carried out. Typical experimental data for  $r = 1.9$  are listed in Table V, as example. Figure 7 shows the results plotted as indicated by eq. (14) [integrated form of eq. (2)]:

$$\ln \frac{r - p}{1 - p} = ak_2' t - \ln 1/r \quad (14)$$

Figure 8 shows the results plotted as indicated by eq. (15) [integrated form of eq. (4)]:

$$C_0 k_2 t = 1/(1 - p) - 1 \quad (15)$$

TABLE V  
Data on Acid-Catalyzed Polyesterification of Nonequimolar Quantities of  
1,3-(Dicarboxymethoxy)benzene with Tetraethylene Glycol<sup>a</sup>

Time (min)	Acid value	$P$	$1/(1 - p)$	$\ln \left( \frac{r - p}{1 - p} \right)$
60	27.25	0.8555	6.92	1.98
90	20.78	0.8898	9.07	2.22
120	10.84	0.9425	17.39	2.81
150	9.36	0.9504	20.16	2.95
180	8.24	0.9556	22.88	3.07
240	5.17	0.9726	36.50	3.52
270	4.67	0.9752	40.32	3.62
330	3.62	0.9808	52.08	3.87
360	3.29	0.9826	57.47	3.97
390	3.04	0.9839	62.11	4.04
420	2.83	0.9850	66.67	4.11
450	2.68	0.9858	70.42	4.16
480	2.49	0.9868	75.76	4.24
510	2.34	0.9876	80.65	4.30
600	2.04	0.9892	92.59	4.43

<sup>a</sup>  $r = 1.9, C_0 = 1.6792 \text{ mol/kg}, [\text{Cat}] = 0.0048 \text{ mol/kg}$ .

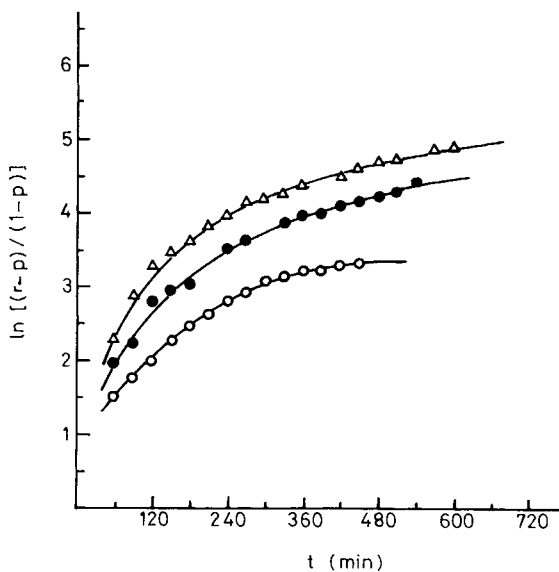


Fig. 7. Plots of  $\ln[(r-p)/(1-p)]$  vs. reaction time  $t$ , for nonequimolar polyesterification reactions of bis-1,3-(Dicarboxymethoxy)benzene with tetraethylene glycol at  $140^{\circ}\text{C}$  in the presence of catalyst ( $[\text{Cat}] = 0.0048 \text{ mol/kg}$ ).  $r$ : (○) 1.6; (●) 1.9; (△) 2.2.

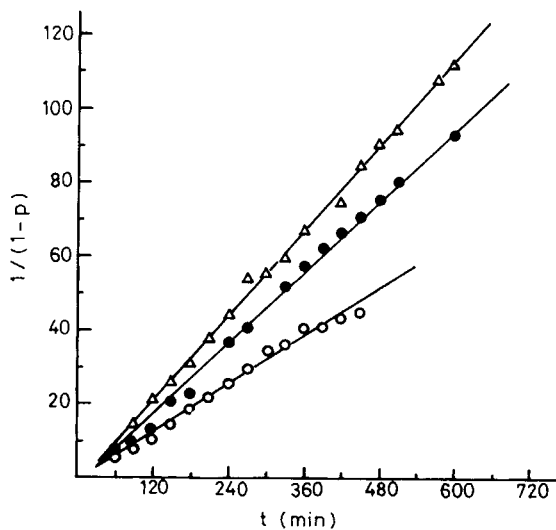


Fig. 8. Plots of  $1/(1-p)$  vs. reaction time  $t$ , for nonequimolar polyesterification reactions of bis-1,3-(Dicarboxymethoxy)benzene with tetraethylene glycol at  $140^{\circ}\text{C}$  in the presence of catalyst ( $[\text{Cat}] = 0.0048 \text{ mol/kg}$ ).  $r$ : (○) 1.6; (●) 1.9; (△) 2.2.

TABLE VI  
Rate Constants ( $k_1$  and  $k_2$ ) for Self-Catalyzed and Acid-Catalyzed Polyesterification Reactions of Nonequimolar Quantities of 1,3-(Dicarboxymethoxy)benzene and Tetraethylene Glycol<sup>a</sup>

$r$ (molar ratio)	$k_1 \times 10^3$ (kg <sup>2</sup> /mol <sup>2</sup> min)	$k_2 \times 10^2$ (kg/mol min)
1.6	13.31 ± 0.32 <sup>b</sup>	5.75 ± 0.20 <sup>c</sup>
1.9		9.86 ± 0.15 <sup>c</sup>
2.0	9.55 ± 1.07 <sup>b</sup>	
2.2		12.51 ± 0.15 <sup>c</sup>
2.5	8.72 ± 0.15 <sup>b</sup>	
3.0	8.22 ± 0.10 <sup>b</sup>	

<sup>a</sup>[Cat] = 0.0048 mol/kg.

<sup>b</sup> $T$  = 160°C.

<sup>c</sup> $T$  = 140°C.

All the results fail to give straight lines with eq. (14), and it is clearly demonstrated that the reactions do not follow the kinetic type of eq. (2) as proposed by Flory but satisfy eq. (4) proposed by Lin and Hsieh, which is a second-order rate equation with respect to the acid.

The rate constants  $k_1$  and  $k_2$  for uncatalyzed and acid-catalyzed reactions at values of  $r$  ranging from 1.6 to 3.0 were evaluated from the slope of the least squares fit regression lines, generated by the method of least squares. The results are shown in Table VI. It was found that in the case of uncatalyzed reactions the value of the rate constant  $k_1$  decreases with increasing  $r$ , while in the case of acid-catalyzed reactions the value of the rate constant  $k_2$  increases with increasing  $r$ . This finding is in agreement with the work of Lin and Yu<sup>14</sup> as well as our previous results.<sup>9,10</sup>

Also the rate constants for polyesterification reactions of cinnamylsuccinic acid with ethylene<sup>9</sup> and butylene<sup>10</sup> glycols are lower than those for polyesterifications of 1,3-(dicarboxymethoxy)benzene with tetraethylene glycol.

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Received February 16, 1988

Accepted September 8, 1988