

Unsaturated Polyesters. III. Kinetics of Polyesterification of Cinnamylsuccinic Acid with Ethylene Glycol

A. F. SHAABAN and M. A. SALEM, *Chemistry Department, Faculty of Science, Zagazig University, Benha Branch, Benha, Egypt* and
N. N. MESSIHA, *Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt*

Synopsis

The polyesterification reactions of cinnamylsuccinic acid with ethylene glycol in both equimolar and nonequimolar ratios were investigated over the temperature range of 130–180°C in the absence and presence of *p*-toluene-sulfonic acid as a catalyst. The kinetic equations were: $-d[\text{COOH}]/dt = k_1[\text{COOH}][\text{OH}]^2$ and $-d[\text{COOH}]/dt = k_2[\text{COOH}]^2$ for uncatalyzed and acid-catalyzed polyesterification reactions, respectively. The apparent rate constants for uncatalyzed and acid-catalyzed reactions were evaluated by using the method of least squares for various values of initial molar ratios between $[\text{OH}]$ and $[\text{COOH}]$. Also, the activation parameters were calculated.

INTRODUCTION

Polyesterification reactions are acid catalyzed as demonstrated by Goldschmidt et al.¹ Accordingly, the following rate equation should hold for polyesterification reactions:

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

where k is the true rate constant and a function of temperature. Kinetics of polyesterification reactions of dicarboxylic acids and diols have been studied extensively, but quite varied results were obtained. The original studies on the kinetics and mechanisms of polyesterification reactions were carried out by Flory.² He concluded that self-catalyzed polyesterifications followed third-order kinetic over the later stages of the reaction according to the following equation:

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

while the acid-catalyzed polyesterification reactions are believed to follow the second-order reaction kinetics:

$$-d[\text{COOH}]/dt = k'_2[\text{COOH}][\text{OH}] \quad (3)$$

where the rate constant k'_2 includes the catalyst concentration. On the other hand, Lin and Hsieh³ reported that the true kinetic behavior of polyesterifica-

tion reaction should be

$$-d[\text{COOH}]/dt = kk_h[\text{COOH}][\text{OH}]^2 = k_1[\text{COOH}][\text{OH}]^2 \quad (4)$$

for uncatalyzed reactions and

$$-d[\text{COOH}]/dt = kK_a/k_h[\text{COOH}]^2 = k_2[\text{COOH}]^2 \quad (5)$$

for acid-catalyzed reactions, where k_h and K_a is the apparent dissociation coefficient and apparent dissociation constant of dicarboxylic acid in glycol, respectively. Chen and Wu⁴ have examined nonequimolar ratio systems and proposed a new kinetic equation. Thus, a variety of conclusions have been reported regarding the kinetic order of the polyesterification reactions. In the present work we reexamined the kinetic plots (for the polyesterification reactions of cinnamylsuccinic acid with ethylene glycol) based on the rate equations provided by Flory² and Lin and Hsieh³ to illustrate the true kinetic behavior of polyesterification reactions.

MATERIALS AND METHODS

Cinnamylsuccinic acid (mp 144°C) was prepared by the reaction of allylbenzene and maleic anhydride according to the method of Christian and Rondestvedt.⁵ Ethylene glycol was fractionally distilled and the fraction, bp 197°C, was collected and used. All solvents used were of reagent grade and were purified by distillation before use.

Bulk polyesterification reaction of cinnamylsuccinic acid with ethylene glycol was carried out under a slow stream of dry deoxygenated nitrogen. Kinetic runs were made at 130–180°C using a thermostatically controlled oil bath. The reaction was followed by titration of the total free carboxyl in sample (≈ 0.2 g dissolved in 20 mL chloroform) removed from the reaction mixture at suitable time intervals, against alcoholic KOH, using phenolphthalein as indicator. Reactions catalyzed by *p*-toluenesulphonic acid were carried out similarly except that the calculated amount of the catalyst ($[\text{Cat}] = 0.0135$ eq/kg) needed for the studied runs was dissolved in glycol in order to keep the catalyst concentration constant, and then the calculated amount of the glycol for each experiment was taken from this mixture. The extent of the reaction (p) or the fraction of the functional groups that reacted at time t was calculated from the equation

$$p = \frac{C'_0 - C'}{C'_0} \quad (6)$$

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

$$\text{DP} = \frac{1 + r}{1 + r - 2p} \quad (7)$$

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

RESULTS AND DISCUSSION

In the present investigation, the equimolar and nonequimolar polyesterification reactions of cinnamylsuccinic acid with ethylene glycol were studied over the temperature range of 130–180°C in the absence and presence of *p*-toluene-sulfonic acid as a catalyst.

**Uncatalyzed and Acid-Catalyzed Polyesterifications of
Equimolar Quantities of Cinnamylsuccinic Acid and Ethylene
Glycol at 130–180°C**

In the polyesterification between equimolar quantities of cinnamylsuccinic acid and ethylene glycol, the experimental data obtained at 180°C are given in Tables I and II for uncatalyzed and acid-catalyzed reactions, respectively. For brevity the analytical data of subsequent experiments at different temperatures for both uncatalyzed and acid-catalyzed reactions are not tabulated. For uncatalyzed polyesterification reactions at various temperatures the relation between $1/(1-p)$ and $1/(1-p)^2$ have been plotted graphically against time using the least squares 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:

$$2C_0^2 k_1 t = 1/(1-p)^2 - 1 \quad (8)$$

where C_0 is the initial concentration of acid. This equation is applicable for both kinetic types of eqs. (2) and (4) in equimolar systems.

TABLE I
Data on Uncatalyzed Polyesterification of Equimolar Quantities
of Cinnamylsuccinic Acid and Ethylene Glycol^a

Time (min)	Acid value	<i>p</i>	$1/(1-p)^2$
30	264.5823	0.3021	2.0532
60	229.8115	0.3938	2.7214
90	210.2601	0.4454	3.2513
120	202.0680	0.4670	3.5201
150	183.8068	0.5152	4.2543
180	173.8923	0.5413	4.7533
210	165.3668	0.5638	5.2561
240	154.4780	0.5925	6.0233
270	148.5405	0.6082	6.5142
300	143.2696	0.6221	7.0025
330	138.3094	0.6352	7.5134
360	131.9826	0.6519	8.2511
390	128.1677	0.6619	8.7499
420	124.6408	0.6712	9.2522
450	121.3300	0.6800	9.7638
480	117.8160	0.6892	10.3546
510	114.2582	0.6986	11.0101
540	111.6931	0.7054	11.5212

^a $C_0 = 6.76$ eq/kg, $T = 180^\circ\text{C}$.

TABLE II
Data on Acid-Catalyzed Polyesterification of Equimolar Quantities
of Cinnamylsuccinic Acid and Ethylene Glycol^a

Time (min)	Acid value	p	$1/(1-p)$
60	123.7827	0.6735	3.0624
90	107.0635	0.7176	3.5417
120	95.2349	0.7488	3.9807
150	87.4251	0.7694	4.3372
180	79.6910	0.7898	4.7566
210	72.1080	0.8098	5.2569
240	66.9905	0.8233	6.6579
270	62.8202	0.8343	6.0342
300	59.1806	0.8439	6.4065
330	55.7686	0.8529	6.7979
360	52.8493	0.8606	7.1737
390	50.1197	0.8678	7.5626
420	48.0724	0.8732	7.8881
450	44.3191	0.8831	8.5522
480	42.6510	0.8875	8.8856
510	39.4664	0.8959	9.6072

^a $C_0 = 6.74$ eq/kg, [Cat] = 0.0135 eq/kg, $T = 180^\circ\text{C}$.

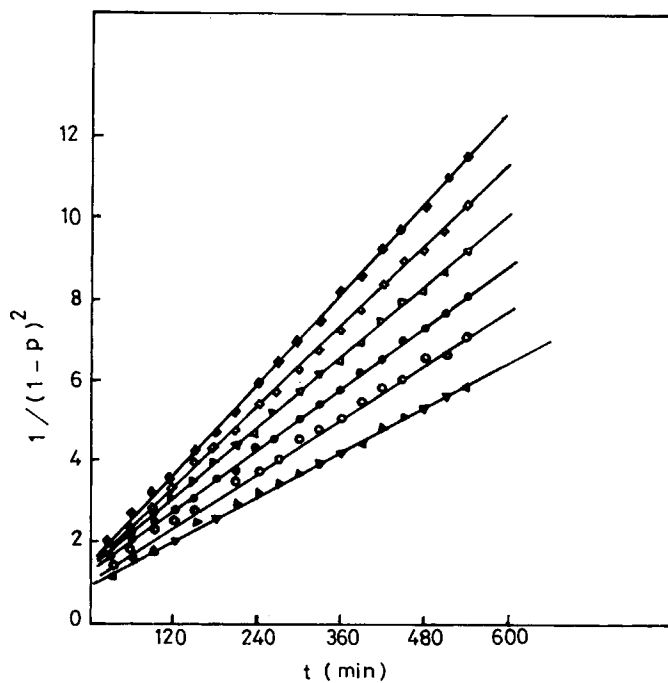


Fig. 1. Plots of $1/(1-p)^2$ vs. reaction time t for equimolar polyesterification reactions of cinnamylsuccinic acid with ethylene glycol at 130 (▲), 140 (○), 150 (●), 160 (△), 170 (□), and 180°C (■) in the absence of catalyst.

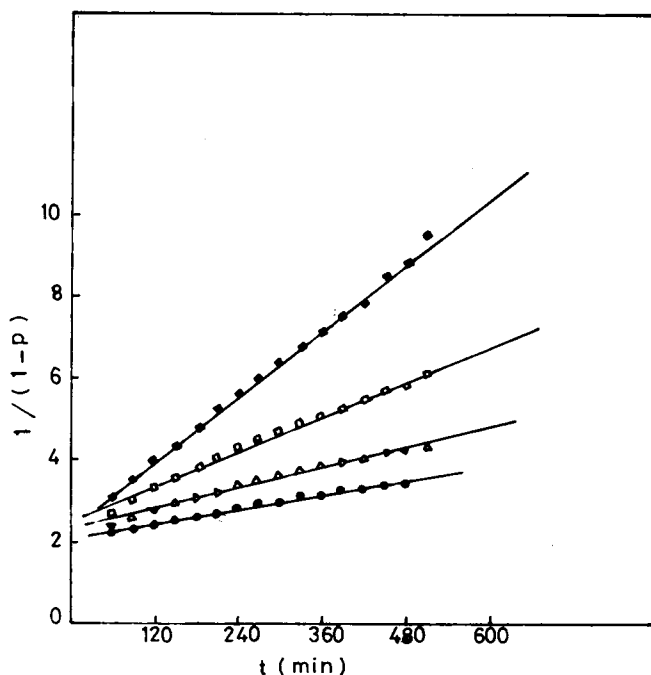


Fig. 2. Plots of $1/(1-p)$ vs. reaction time t for equimolar polyesterification reactions of cinnamylsuccinic acid with ethylene glycol at 150 (●), 160 (△), 170 (□), and 180°C (■) in the presence of catalyst.

For the acid-catalyzed polyesterification reactions at various temperatures the relation between $1/(1-p)$ and $1/(1-p)^2$ have been plotted graphically against time using the least squares method. The best linear plots were obtained by plotting $1/(1-p)$ vs. time (Fig. 2), indicating that the reaction satisfies the second-order rate equation [eq. (9)], which is applicable for both kinetic types of eqs. (3) and (5) in equimolar systems:

$$C_0 k_2 t = 1/(1-p) - 1 \quad (9)$$

The apparent rate constants k_1 and k_2 for both the uncatalyzed and acid-catalyzed polyesterification reactions have been calculated and are presented in Table III.

The activation parameters (E_a^* , ΔH^* , and ΔS^*) were calculated making use of transition state theory equation.^{6,7} The results of calculating the activation parameters for uncatalyzed and acid-catalyzed polyesterification reactions of cinnamylsuccinic acid with ethylene glycol in equimolar quantities at 180°C are illustrated in Table IV. The Arrhenius equation was found to obeyed satisfactory since good straight lines were obtained when $\ln k_1$ and $\ln k_2$ were plotted vs. $1/T$, as shown in Figure 3.

It appears that the rate constants for the acid-catalyzed polyesterification reactions are characterized by higher values than the corresponding uncatalyzed ones, in spite of the fact that the activation energy is less in the former case. These results are in agreement with the similar results obtained by

TABLE III
Apparent Rate Constants (k_1 and k_2) for Uncatalyzed and Acid-Catalyzed Polyesterification Reactions of Equimolar Quantities of Cinnamylsuccinic Acid and Ethylene Glycol^a

Temp (°C)	Apparent rate constants	
	$k_1 \times 10^5$ (kg ² /(eq mol) ² min)	$k_2 \times 10^4$ (kg/eq mol min)
130	9.85 ± 0.11	—
140	11.56 ± 0.11	—
150	13.82 ± 0.09	4.50 ± 0.31
160	15.63 ± 0.13	6.69 ± 0.37
170	17.86 ± 0.18	11.45 ± 0.42
180	20.29 ± 0.14	21.03 ± 0.36

^a[Cat] = 0.0135 eq/kg.

TABLE IV
Activation Parameters for Uncatalyzed and Acid-Catalyzed Polyesterification of Equimolar Quantities of Cinnamylsuccinic Acid and Ethylene Glycol at 180°C

	E_a^* (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔS^* (J K ⁻¹ mol ⁻¹)
Uncatalyzed	21.93 ± 0.46	18.15 ± 0.46	-279.08 ± 1.02
Acid-catalyzed	82.04 ± 6.60	78.28 ± 6.60	-126.90 ± 14.57

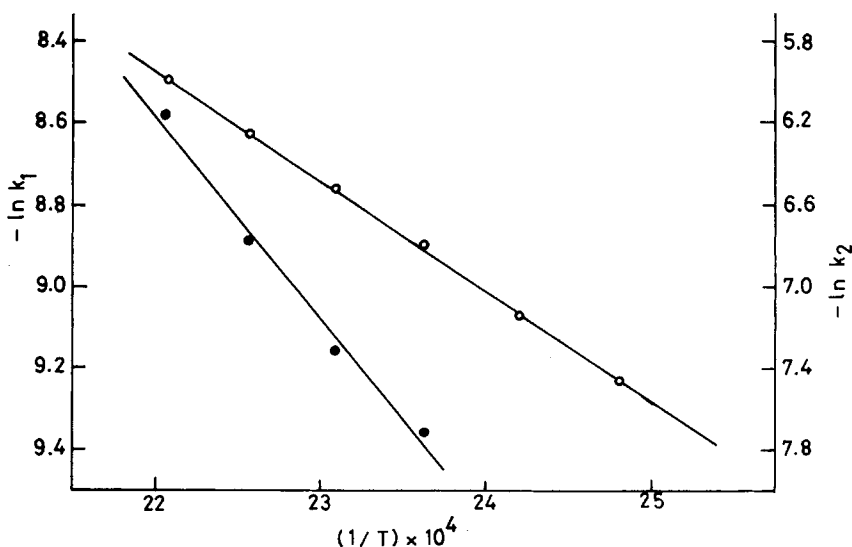


Fig. 3. Plots of $\ln k_1$ and $\ln k_2$ vs. $1/T$ for (O) uncatalyzed and (●) acid-catalyzed polyesterification reactions of cinnamylsuccinic acid with ethylene glycol in equimolar quantities.

Baddar et al.^{8,9} as well as the results obtained in our previous work.¹⁰ This indicates that the frequency factor in the Arrhenius equation is much greater for the reaction involving a charged catalyst as indicated by the increase in the entropy of activation (ΔS^*) by about 150 J K mol^{-1} in the catalyzed polyesterification reactions. The low negative values of ΔS^* may be due to the higher viscosity of the reaction medium.

Uncatalyzed Polyesterification of Nonequimolar Quantities of Cinnamylsuccinic Acid and Ethylene Glycol at 180°C

The typical experimental data of the polyesterification between nonequimolar quantities of cinnamylsuccinic acid and ethylene glycol when $r = 1.9$ in the absence of catalyst at constant temperature of 180°C are listed in Table V as an example. Other analytical data of subsequent experiments under various r values ($r = 1.3, 1.6,$ and 2.2) are not tabulated.

All the results obtained were plotted as indicated by eq. (10) [integrated form of eq. (2)] as shown in Figure 4:

$$\frac{r-1}{1-p} - \ln \frac{r-p}{1-p} = a^2 k_1 t + \frac{a}{C_0} - \ln r \quad (10)$$

where $a = (r-1)C_0$. On the other hand, the results plotted as indicated by eq. (11) [the integrated form of eq. (4)] are shown in Figure 5:

$$\ln \frac{r-p}{1-p} - \frac{r-1}{r-p} = a^2 k_1 t + \ln r - (r-1)/r \quad (11)$$

At first glance, the data seem fairly well represented by eq. (11) rather than

TABLE V
Data on Uncatalyzed Polyesterification of Nonequimolar Quantities of Cinnamylsuccinic Acid and Ethylene Glycol^a

Time (min)	Acid value	p	$\frac{r-1}{1-p} - \ln \frac{r-p}{1-p}$	$\ln \frac{r-p}{1-p} - \frac{r-1}{r-p}$
60	80.7930	0.7466	2.0365	0.7353
120	39.9981	0.8745	5.0738	1.2234
180	23.7440	0.9255	9.5150	1.6480
240	14.8201	0.9535	16.3506	2.0629
300	9.7207	0.9695	26.1042	2.4512
360	6.5336	0.9795	40.1189	2.8272
420	4.6213	0.9855	57.9542	3.1606
480	3.3465	0.9895	81.2920	3.4746
540	2.0717	0.9935	123.5872	3.9454
600	1.7531	0.9945	158.6066	4.1103
660	1.1154	0.9965	251.6992	4.5578
720	0.7968	0.9975	354.2548	4.8921
780	0.4781	0.9985	593.8011	5.4006

^a $r = 1.9, C_0 = 5.68 \text{ eq/kg}, T = 180^\circ\text{C}, \text{DP from } 1.0000 \text{ to } 3.2115.$

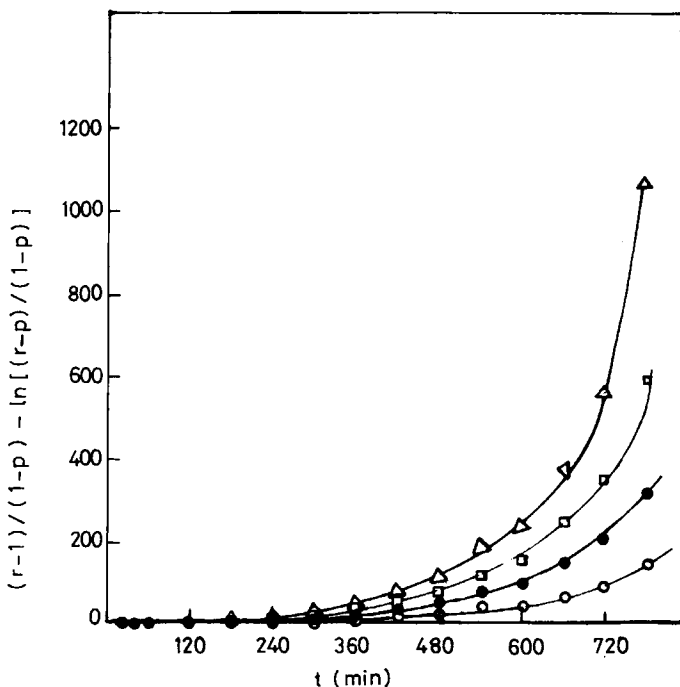


Fig. 4. Plots of $(r-1)/(1-p) - \ln[(r-p)/(1-p)]$ vs. reaction time t , for nonequimolar polyesterification reactions of cinnamylsuccinic acid with ethylene glycol at 180°C , in the absence of catalyst. $r =$ (○) 1.3; (●) 1.6; (□) 1.9; (Δ) 2.2.

eq. (10) over the range of $p = 0$ up to $p = 0.99$. Evidently, these are third-order kinetics not according to eq. (2) proposed by Flory,² but eq. (4) proposed by Lin and Hsieh.³ The correspondence between theory and data in Flory's experiments can be regarded as fortuity of an equimolar reaction, to which eq. (12) is applicable for both kinetic types of eqs. (2) and (4):

$$-dC/dt = kC^3 \quad (12)$$

The nonequimolar polyesterification reactions of cinnamylsuccinic acid with ethylene glycol in the absence of catalyst for a large molar ration ($r = 5$) was studied. The experimental conditions and results are illustrated in Table VI. The results indicate a linear relationship when it is plotted only on the basis of eq. (13), instead of eq. (4):

$$-d[\text{COOH}]/dt = k_3[\text{COOH}]^2 \quad (13)$$

This means that the reaction is now second-order with respect to $[\text{COOH}]$. Figure 6 shows the typical data for uncatalyzed system in the case of excess in ethylene glycol, which is plotted as indicated by eq. (14) [integrated form of eq. (13)]:

$$C_0 k_3 t = 1/(1-p) - 1 \quad (14)$$

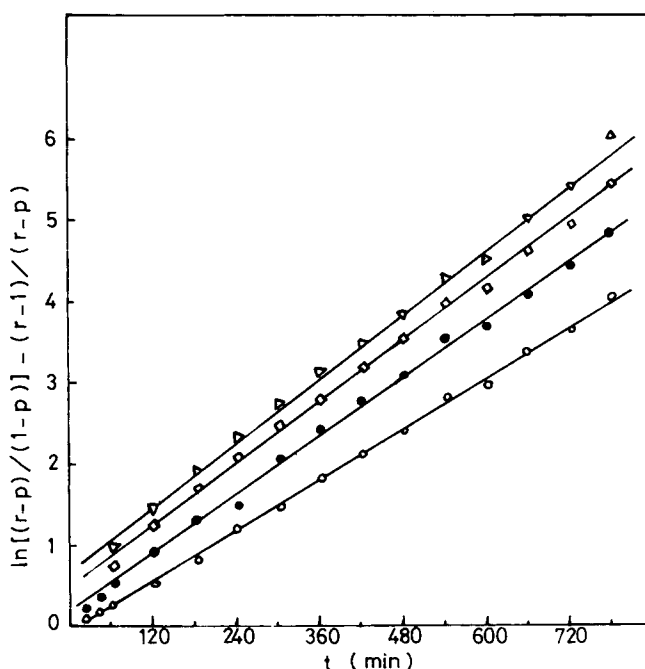


Fig. 5. Plots of $\ln[(r-p)/(1-p)] - (r-1)/(r-p)$ vs. reaction time t , for nonequimolar polyesterification reactions of cinnamylsuccinic acid with ethylene glycol at 180°C in the absence of catalyst. $r = (\circ) 1.3; (\bullet) 1.6; (\square) 1.9; (\triangle) 2.2$.

TABLE VI
Data on Uncatalyzed Polyesterification of Cinnamylsuccinic Acid
with Excess of Ethylene Glycol^a

Time (min)	Acid value	p	$1/(1-p)$
15	63.1231	0.6938	3.2658
30	20.615	0.9000	10.0000
45	12.8844	0.9375	16.0000
60	9.3798	0.9545	21.9780
90	5.8959	0.9714	34.9650
120	4.3910	0.9787	46.9484
150	3.4427	0.9833	59.8802
180	2.7830	0.9865	74.0741
210	2.4326	0.9882	84.7458
240	2.1233	0.9897	97.0874
270	1.8759	0.9909	109.8901

^a $r = 5, C_0 = 3.67 \text{ eq/kg}, T = 180^{\circ}\text{C}$.

Acid-Catalyzed Polyesterification of Nonequimolar Quantities of Cinnamylsuccinic Acid and Ethylene Glycol at 180°C

Several experiments on the reaction of cinnamylsuccinic acid with ethylene glycol catalyzed by small amount of *p*-toluene-sulfonic acid at 180°C in nonequimolar ratios ($r = 1.3, 1.6, 1.9$, and 2.2) were carried out. The typical experimental data of $r = 1.9$ are listed in Table VII, as an example. Figure 7

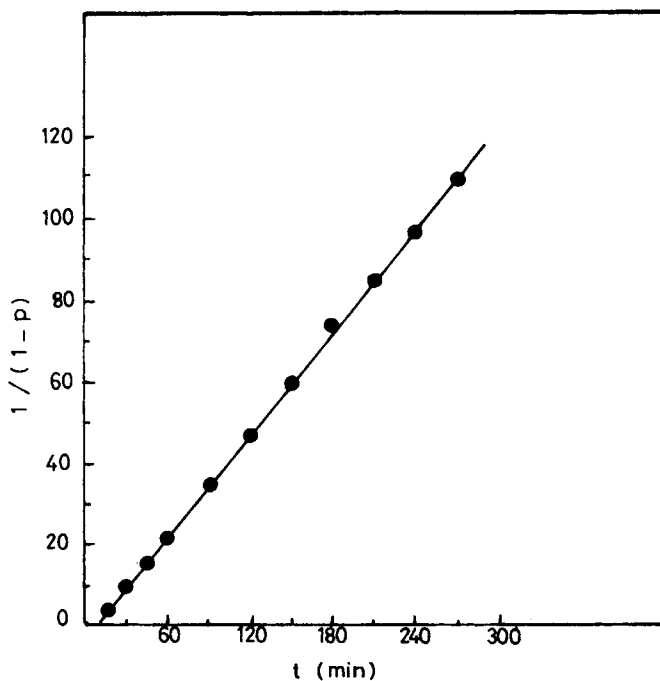


Fig. 6. Plot of $1/(1-p)$ vs. reaction time t , for nonequimolar polyesterification reaction of cinnamylsuccinic acid with excess of ethylene glycol ($r = 5$) at 180°C in the absence of catalyst.

TABLE VII
Data on Acid-Catalyzed Polyesterification of Nonequimolar Quantities
of Cinnamylsuccinic Acid and Ethylene Glycol^a

Time (min)	Acid value	p	$\frac{1}{1-p}$	$\ln \frac{r-p}{1-p}$
0	318.8675	0.0000	1.0000	0.6419
30	18.2712	0.9427	17.4456	2.8155
60	12.5635	0.9606	25.3682	3.1710
90	8.4500	0.9735	37.7694	3.5552
120	6.5049	0.9796	48.9735	3.8083
150	5.1019	0.9840	62.6374	4.0496
180	4.5279	0.9858	70.2315	4.1621
240	3.4119	0.9893	93.2455	4.4417
300	2.7741	0.9913	115.3422	4.6522
360	2.3915	0.9925	133.4268	4.7965
420	1.9769	0.9938	160.1026	4.9773
480	1.7856	0.9944	178.5021	5.0854
540	1.5943	0.9950	200.0568	5.1988

^a $r = 1.9$, $C_0 = 5.66$ eq/kg, $[\text{Cat}] = 0.0135$ eq/kg, $T = 180^{\circ}\text{C}$, DP from 1.000 to 3.1868.

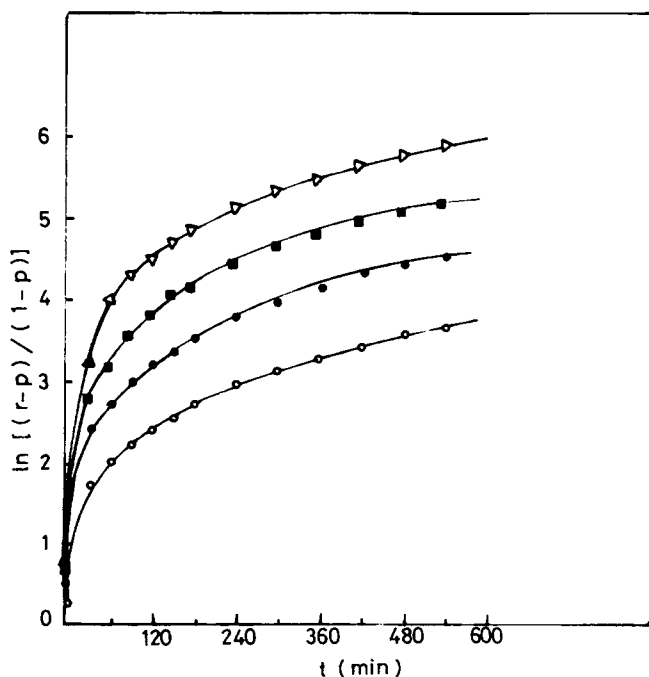


Fig. 7. Plots of $\ln[(r-p)/(1-p)]$ vs. reaction time t , for nonequimolar polyesterification reactions of cinnamylsuccinic acid with ethylene glycol at 180°C in the presence of catalyst. $[\text{Cat.}] = 0.0135 \text{ eq/kg}$ $r = (\circ) 1.3; (\bullet) 1.6; (\blacksquare) 1.9; (\Delta) 2.2$.

show the results plotted as indicated by eq. (15) [the integrated form of eq. (3)]:

$$\ln \frac{r-p}{1-p} = ak_2't - \ln \frac{1}{r} \quad (15)$$

Figure 8 shows the results plotted as indicated by eq. (16) [the integrated form of eq. (5)]:

$$C_0 k_2 t = 1/(1-p) - 1 \quad (16)$$

All the results fail to give straight lines with eq. (15), and it is clearly demonstrated that the reaction do not follow the kinetic type of eq. (3) as proposed by Flory but of eq. (5) proposed by Lin and Hsieh, which is a second-order rate equation with respect to the acid.

The apparent rate constants k_1 and k_2 for both uncatalyzed and acid-catalyzed reactions at various values of r ranging from 1.3 to 2.2 were evaluated from the slope of the best-fit regression lines, which were generated from the experimental data for all cases by the method of least squares. The results are shown in Table VIII. It was found that in the case of uncatalyzed reactions the value of the apparent rate constant k_1 decreases with increasing r values, while in the case of acid-catalyzed reactions the value of the apparent rate constant k_2 increases with increasing r . This finding is in agreement with the work of Lin and Yu.¹¹ These phenomena can be attributed to the depression

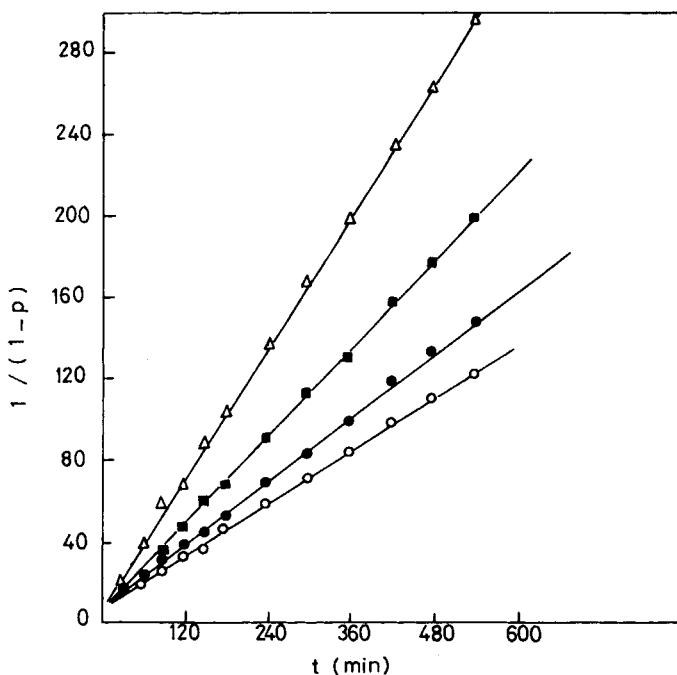


Fig. 8. Plots of $1/(1-p)$ vs. reaction time t , for nonequimolar polyesterification reactions of cinnamylsuccinic acid with ethylene glycol at 180°C , in the presence of catalyst. $[\text{Cat.}] = 0.0135$ eq/kg $r = (\text{O}) 1.3; (\bullet) 1.6; (\blacksquare) 1.9; (\Delta) 2.2$.

of the apparent dissociation coefficient of cinnamylsuccinic acid (k_h) in ethylene glycol with increasing r at constant temperature according to

$$[\text{H}^+] = k_h[\text{OH}] \quad (17)$$

Since $k_1 = k k_h$ according to eq. (4), the apparent rate constant k_1 , for the uncatalyzed nonequimolar systems would decrease with increasing r , because the value of k would remain constant at the given temperature. Also, $k_2 = kK_a/k_h$ according to eq. (5) and k_2 would increase with increasing r , because k and K_a would all remain at constant value at a given temperature.

TABLE VIII
Apparent Rate Constants (k_1 and k_2) for Uncatalyzed and Acid-Catalyzed Polyesterification Reactions of Nonequimolar Quantities of Cinnamylsuccinic Acid and Ethylene Glycol^a

r (molar ratio)	Apparent rate constants	
	$k_1 \times 10^4$ ($\text{kg}^2/(\text{eq mol})^2 \text{ min}$)	$k_2 \times 10^2$ ($\text{kg}/\text{eq mol min}$)
1.3	14.22 ± 0.13	3.47 ± 0.04
1.6	4.60 ± 0.07	4.46 ± 0.06
1.9	2.44 ± 0.04	6.43 ± 0.06
2.2	1.63 ± 0.03	10.10 ± 0.09

^a $[\text{Cat.}] = 0.0135$ eq/kg, $T = 180^{\circ}\text{C}$.

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