The Kinetics of Polyesterification. III. A Mathematical Model for Quantitative Prediction of the Apparent Rate Constants

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Synopsis

A mathematical model for the apparent constants k_1 and k_2 which presents a quantitative explanation of the observed kinetic behavior in both uncatalyzed and acid-catalyzed polyesterification between ethylene glycol and a dibasic acid in different initial molar ratios was developed. This model consists of two types of similar semiempirical equations, one of which applies to the uncatalyzed reaction and the other to the acid-catalyzed reaction. They are both based on the same apparent dissociation coefficient, k_h, of a dibasic acid in ethylene glycol, which can be expressed as $k_h = K e^{-ar}$ at constant temperature. The symbol a in the equation represents the sensitivity constant to change in the initial molar ratio $r = [OH]_0/[COOH]_0$. The value of the true rate constant for polyesterification between succinic acid and ethylene glycol at 195°C was estimated to be 3.02×10^{-3} [in kg²/(equiv. moles)²·min] based on this model.

INTRODUCTION

Many experimental studies on the polyesterification between dibasic acids and glycols have been reported. Among these, the typical data obtained by Flory[1] are quite general and often suffice for our discussion. Esterification reactions are acid catalyzed as demonstrated by Goldschmidt.[2] Accordingly, the following rate equation should also hold for polyesterifications:

$$-d[COOH]/dt = k[COOH][OH][H^+] \qquad (1)$$

where k is the true rate constant and a function of temperature. Unfortunately, kinetic data in the literature are meager. A common impression on the correspondence between theory and data of Flory may be caused by the experiments with equimolar reactants. Recently, however, it has been shown[3,4] that the true kinetic behavior of polyesterifications should be

$$-d[COOH]/dt = k_1[COOH][OH]^2 \qquad (2)$$

for uncatalyzed reactions and

$$-d[COOH]/dt = k_2[COOH]^2 \qquad (3)$$

for acid-catalyzed reactions. Here, k_1 of eq. (2) and k_2 of eq. (3) are the apparent rate constants. According to our dissociation-controlling mechanism,[4] it has been shown that

$$k_1 = kk_h \qquad \left[\frac{kg^2}{(\text{equiv. moles})^2 \cdot \text{min}}\right] \qquad (4)$$

and

$$k_2 = kK_a/k_h \qquad \left[\frac{kg}{(\text{equiv. moles}) \cdot \text{min}}\right] \qquad (5)$$

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where K_a is the apparent acid dissociation constant and is a function of temperature, and k_h is the apparent dissociation coefficient of a dibasic acid in ethylene glycol, which is a function of both the temperature and the initial molar ratio $r = [OH]_0/[COOH]_0$. It is, therefore, possible that limited dissociation of dibasic acid in ethylene glycol may be responsible for the apparent kinetic behavior of polyesterification. This new theory on the mechanism of polyesterification has been proved by our previous data.[3,4] A mathematical model is developed in this paper to present a quantitative explanation of the kinetic behavior of polyesterification observed.

EXPERIMENTAL

The materials and the apparatus as well as the procedure of the experiment were same as those previously described.[3,4]

THEORETICAL TREATMENT

As previously defined,[4] k_h is the number of moles of hydrogen ion dissociated from a dibasic acid per 0.5 mole ethylene glycol. The authors have shown that k_h decreases as the value of r increases.[4] It is easily recognized that k_h would approach zero when r becomes infinity. Hence, k_h can be expressed as a function of both temperature and r as follows:

$$
\begin{aligned}
k_h &= f(T_c,r) \\
&= (A \cdot e^{-\Delta E/RT_c}) \, e^{-ar} \\
&= K \, e^{-ar}
\end{aligned}
\tag{6}
$$

where T_c is a certain constant temperature; R is the gas constant; A is the probability factor; ΔE is the activation energy; a is the sensitivity constant, a measure of the sensitivity of k_h to the change in r; and $K = A \cdot e^{-\Delta E/RT_c}$ is a constant at T_c.

By combining eqs. (4), (5), and (6), k_1 and k_2 are then given, respectively, by

$$
k_1 = kK \cdot e^{-ar} = K_1 \cdot e^{-ar}
\tag{7}
$$

and

$$
k_2 = (kK_a/K) \cdot e^{ar} = K_2 \cdot e^{ar}
\tag{8}
$$

where $K_1 = kK$ and $K_2 = kK_a/K$ are all constants at a given temperature.

By taking the natural logarithm on each side of the above equations, they yield

$$
\ln k_1 = \ln K_1 - ar = K_1' - ar
\tag{9}
$$

and

$$
\ln k_2 = \ln K_2 + ar = K_2' + ar
\tag{10}
$$

where $K_1' = \ln K_1$ and $K_2' = \ln K_2$ are also constants.

It can readily be shown that a plot of $\ln k_1$ versus r would give a straight line with slope $-a$ and intercept K_1', while that of $\ln k_2$ versus r would give another with slope $+a$ and intercept K_2'. By combining eqs. (9) and (10), we get

$$
\ln k_1 + \ln k_2 = \ln (k_1 k_2) = K_1' + K_2' = K_3'
\tag{11}
$$

or

$$k_1 k_2 = K_3 \tag{12}$$

where $K_3' = K_1' + K_2'$ and $K_3 = e^{K_3'} = K_1 K_2 = k^2 K_a$ are all constants. This implies that at a certain temperature the product of the apparent rate constants k_1 and k_2 under any value of r should remain constant theoretically.

RESULTS AND DISCUSSION

Succinic Acid–Ethylene Glycol System

The experimental data of the apparent rate constants k_1 and k_2 for the succinic acid–ethylene glycol system at a constant temperature of 195°C are listed in column 2 of Table I. The general semiempirical equations for 195°C obtained by linear regression of the values of $\ln k_1$ or $\ln k_2$ on the values of r are given by

$$\ln k_1 = -3.8993 - 2.6r \quad \text{or} \quad k_1 = 2.03 \times 10^{-2} \cdot e^{-2.6r} \tag{13}$$

and

$$\ln k_2 = -7.1372 + 2.6r \quad \text{or} \quad k_2 = 7.95 \times 10^{-4} \cdot e^{2.6r} \tag{14}$$

In fact, we obtained the same value of 2.6 for the sensitivity constant a in both cases, as shown in Table I and Figure 1.

Table II shows the values of $\ln(k_1 k_2)$ for different values of r. It can be seen that they all closely keep at a constant value of about -11, as could be expected from eq. (11). By combining eqs. (13) and (14), we also get

$$\ln(k_1 k_2) = K_3' = -11.0365 \tag{15}$$

and

$$k_1 k_2 = K_3 = k^2 K_a = 1.61 \times 10^{-5} \tag{16}$$

TABLE I
Apparent Rate Constants k_1 and k_2 for Succinic Acid–Ethylene Glycol System at $T = 195$°C

(a) For Uncatalyzed Reactions			
r	k_1, $\dfrac{\text{kg}_2}{\text{(equiv. moles)}^2 \cdot \text{min}}$	$\ln k_1$	Parameters[a] in eq. (9)
1.0	1.80×10^{-3}	-6.3200	$K_1' = -3.8993$
1.3	4.60×10^{-4}	-7.6843	$-a = -2.6$
1.6	3.88×10^{-4}	-7.8545	

(b) For Acid–Catalyzed Reactions[b]			
r	k_2, $\dfrac{\text{kg}^2}{\text{(equiv. moles)}^2 \cdot \text{min}}$	$\ln k_1$	Parameters[a][c] in eq. (10)
1.3	2.27×10^{-2}	-3.7854	$K_2' = -7.1372$
1.6	4.92×10^{-2}	-3.0119	$+a = -2.6$

[a] Obtained by linear regression of $\ln k_1$ on r using method of least squares.

[b] The datum of k_2 at $r = 1.0$ is omitted because due to diffusion-controlling mechanism[4] it is less meaningful.

[c] Also obtained by using method of least squares, but at this time it is equivalentsto finding the solution of two simultaneous equations for these two unknown parameters.

for average values. Hence, at 195°C, if we know the value of either k_1 or k_2 at a given value of r, we can then calculate that of the other by using eq. (16). Furthermore, if we know the value of the apparent acid dissociation constant K_a at 195°C, we can also estimate the value of the true rate constant k for polyesterification at the same temperature. Based on our data,[4] k_h for the succinic acid–ethylene glycol system at 195°C was calculated to be

$$k_h = \frac{[H^+]}{[OH]} = 0.13 \quad \left[\frac{\text{mole } H^+}{0.5 \text{ mole ethylene glycol}} \right]$$

$$= 0.13 \left[\frac{\text{mole } H^+}{(0.5 \text{ mole ethylene glycol})(62.06 \text{ g/mole})/(1000 \text{ g/kg})} \right]$$

$$= 4.19 \text{ [moles } H^+/\text{kg ethylene glycol]}$$

$$\cong 4.19 \text{ [moles } H^+/\text{kg solution]} \tag{17}$$

This indicates that the saturated solution of succinic acid in ethylene glycol at 195°C contains about 4.19 moles H^+ dissociated from succinic acid per kg ethylene glycol or, approximately, per kg solution. Hence, we may assume $[H^+]$ = $[COO^-] \cong 4.19$ equiv. moles/kg in the above saturated solution. If the order of magnitude of the concentration of the carboxyl groups is 10^1, i.e., $[COOH] \cong$ 10 equiv. moles/kg, the apparent acid dissociation constant can be estimated as follows:

$$K_a = \frac{[H^+][COO^-]}{[COOH]} \cong \frac{4.19^2}{10} = 1.76 \quad \left[\frac{\text{equiv. moles}}{\text{kg}} \right] \tag{18}$$

With eq. (16), we can estimate the true rate constant for polyesterification between succinic acid and ethylene glycol at 195°C to be
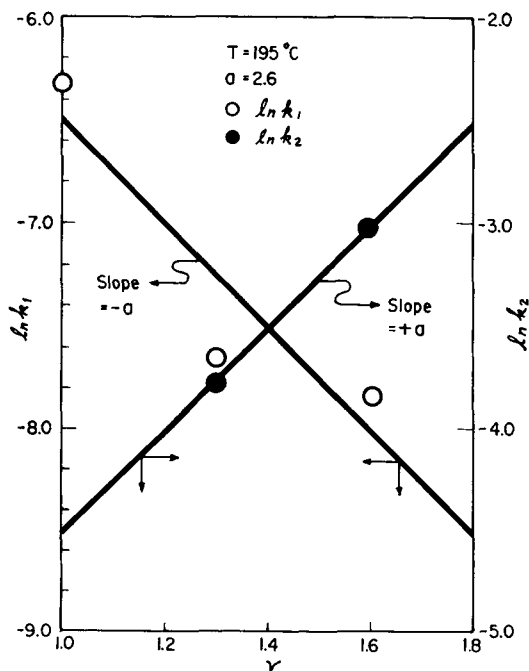

Fig. 1. Plots of ln k_1 and ln k_2 vs r for succinic acid–ethylene glycol system. Two straight lines with slopes ±2.6 are obtained.

TABLE II
Product of the Apparent Rate Constants k_1 and k_2 for the Succinic Acid–Ethylene Glycol
System[a] at $T = 195°C$

r	$k_1, \dfrac{\text{kg}^2}{(\text{equiv. moles})^2 \cdot \text{min}}$	$k_2, \dfrac{\text{kg}}{(\text{equiv. moles}) \cdot \text{min}}$	$\ln k_1$	$\ln k_2$	$\ln (k_1 k_2)$
1.0	1.80×10^{-3}	5.58×10^{-3} [b]	-6.3200	-5.1886	-11.5086
1.3	4.60×10^{-4}	2.27×10^{-2}	-7.6843	-3.7854	-11.4697
1.6	3.88×10^{-4}	4.92×10^{-2}	-7.8545	-3.0119	-10.8664

[a] In comparison, the value in eq. (15) is $\ln (k_1 k_2) = -11.0365$.
[b] This value is the apparent rate constant based on the initial rate of the acid-catalyzed equimolar reaction, as given in our previous paper,[4] rather than based on the averaged rate calculated by linear regression over the entire reaction period.

$$k = (k_1 k_2/K_a)^{1/2} \cong (1.61 \times 10^{-5}/1.76)^{1/2}$$

$$= 3.02 \times 10^{-3} \quad \left[\frac{\text{kg}^2}{(\text{equiv. moles})^2 \cdot \text{min}} \right] \quad (19)$$

Adipic Acid–Ethylene Glycol System

The experimental data of the apparent rate constants k_1 at 180°C and k_2 at 160°C for the adipic acid–ethylene glycol system are listed in column 2 of Table III. Because these data for the two different cases—uncatalyzed and acid catalyzed—are not measured at the same temperature, the results obtained cannot readily be used for further estimation of the true rate constant k. But the value of a, the measure of the sensitivity of k_h to the change in r, can still be obtained by the same way as was done for the succinic acid–ethylene glycol system. The plots are shown in Figure 2, and the final semiempirical equations obtained are

$$\ln k_1 = -4.8133 - 2.0r \quad \text{or} \quad k_1 = 8.12 \times 10^{-3} \cdot e^{-2.0r} \quad (20)$$

at 180°C and

TABLE III
Apparent Rate Constants k_1 and k_2 for Adipic Acid–Ethylene Glycol System

(a) For Uncatalyzed Reactions at $T = 180°C$

r	$k_1, \dfrac{\text{kg}^2}{(\text{equiv, moles})^2 \cdot \text{min}}$	$\ln k_1$	Parameters[a] in eq. (9)
1.0	1.47×10^{-3}	-6.5245	
1.2	6.21×10^{-4}	-7.3842	$K_1' = -4.8133$
1.6	2.76×10^{-4}	-8.1951	$-a = -2.0$
2.2	1.22×10^{-4}	-9.0082	

(b) For Acid-Catalyzed Reactions at $T = 160°C$

r	$k_2, \dfrac{\text{kg}^2}{(\text{equiv. moles})^2 \cdot \text{min}}$	$\ln k_1$	Parameters[a] in eq. (10)
1.2	2.29×10^{-2}	-3.7784	$K_2' = -5.9392$
1.6	8.90×10^{-2}	-2.4188	$+a = +2.0$
2.0	1.10×10^{-1}	-2.2100	

[a] Obtained by linear regression of $\ln k_1$ (or $\ln k_2$) on r by using method of least squares.
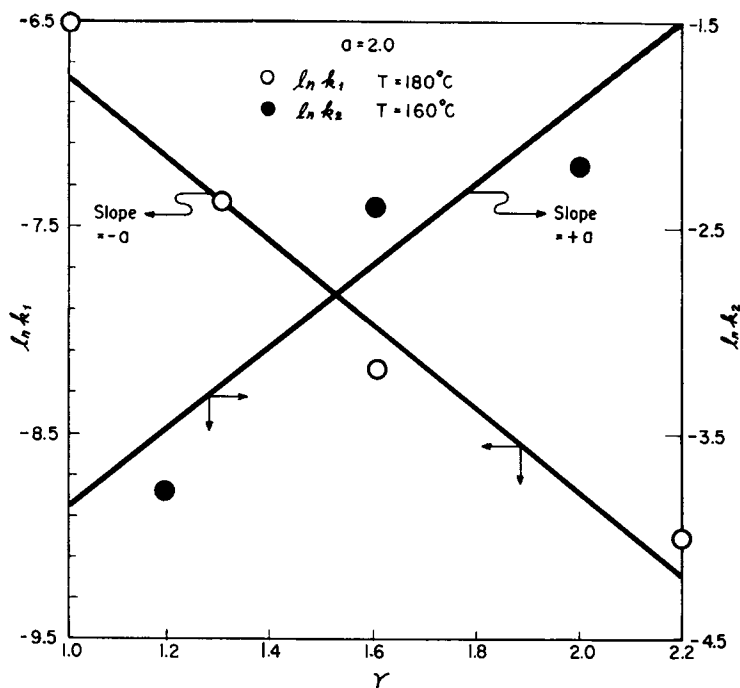
Fig. 2. Plots of $\ln k_1$ and $\ln k_2$ vs r for adipic acid–ethylene glycol system. Two straight lines with slopes ± 2.0 are obtained.

$$\ln k_2 = -5.9392 + 2.0r \qquad \text{or} \qquad k_2 = 2.63 \times 10^{-3} \cdot e^{2.0r} \qquad (21)$$

at 160°C. In fact, we obtained the same value of 2.0 for the sensitivity constant a in both cases, as shown in Table III and Figure 2.

CONCLUSIONS

According to the dissociation-controlling mechanism, we assume k_h to be a function of two separable variables T and r, as shown in eq. (6). Based on our experimental data, it is found that the model is quite satisfactory for these two systems studied. They are valuable for the estimation of k_1 and k_2 when exact experimental values are not available.

The values of the sensitivity constant a are 2.6 for the succinic acid–ethylene glycol system and 2.0 for the adipic acid–ethylene glycol system. This implies that the values of the apparent rate constants k_1 and k_2 are more sensitive to the change in r for the former system than for the latter one. In other words, same magnitude of change in r would cause larger changes in k_1 and k_2 for the former than for the latter system.

It must be pointed out that in this model the value of r should always be greater than, or equal to, unity. It should also not be greater than about 4 for the adipic acid–ethylene glycol system and about 12 for the succinic acid–ethylene glycol system, because under these conditions the kinetic behavior would no longer obey the rate equation (2) for the uncatalyzed polyesterification.[3,4]

According to eq. (6), the other variable, namely, temperature T, can also be taken into account with the model if we perform experiments at certain different

temperatures to obtain the apparent rate constants k_1 and k_2. We can then find the values of such constants as A and ΔE. The model can be extended to predict the values of k_1 and k_2 for any value of r and T.

References

1. P. J. Flory, *J. Am. Chem. Soc.*, **59,** 466 (1937); *ibid.*, **61,** 3334 (1939).
2. H. Goldschimidt, *Z. Phys. Chem.*, **60,** 728 (1907); *ibid.*, **70,** 627 (1910); *ibid.*, **81,** 30 (1913).
3. C. C. Lin and K. H. Hsieh, *J. Appl. Polym. Sci.*, **21,** 2711 (1977).
4. C. C. Lin and P. C. Yu, *J. Polym. Sci.*, to appear.