

Kinetics of Reaction of C₃₆ Dimer Acids with Diethylenetriamine and Triethylenetetramine for Reactive Polyamides*

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SYNOPSIS

Kinetic studies were carried out on the reaction between C₃₆ dimer acids and diethylenetriamine (DETA) and triethylenetetramine (TETA) in melt phase. The reactions were performed at temperatures in the range of 145° to 190°C and followed by determination of the acid and amine values of the intermittent products. The polyamidation reactions of C₃₆ dimer acids and DETA and TETA followed overall second-order kinetics and had activation energies of 14.4 kcal/g mol and 12.3 kcal/g mol, respectively. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Fatty dicarboxylic acids on reaction with ethylenediamine give nonreactive polyamides^{1,2} and, on reaction with polyamines such as diethylenetriamine (DETA) and triethylenetetramine (TETA), give reactive polyamides that contain mainly secondary amino groups for further reaction.^{3,7} The reactive polyamides are used extensively for reaction with epoxy and phenolformaldehyde resins to yield adhesives that are useful in coatings and laminating, in structural work for patching and sealing compounds, and for protective coatings.^{3,7} The reactive polyamides derived from C₃₆ dimer acids are commercially employed as curing agents for epoxy resins.^{4,5} The utilization of C₁₉ diacid-based reactive polyamides as epoxy curing agents has been reported.⁶ Reactive polyamides⁸ were also prepared from C₂₁ diacids that were derived from dehydrated castor oil fatty acids and acrylic acid.⁹ Recently, we have reported kinetics of reaction of ethylenediamine with C₃₆ dimer acids^{10,11} and C₂₁ diacids¹² to get nonreactive polyamides. There is no reported

literature on the study of kinetics of the polyamidation reaction for the reactive polyamides. In the present work, kinetics of reaction of C₃₆ dimer acids with DETA and TETA to get reactive polyamides was studied. The reactive polyamides on curing with epoxy and phenol formaldehyde resins yields cross-linked products with better adhesive strength.

EXPERIMENTAL

Materials

C₃₆ Dimer acids (Empol 1010 grade; acid value, 198 mg KOH/g and purity, 97%) were used. Diethylenetriamine (DETA), triethylenetetramine (TETA), and other chemicals and solvents used were of reagent grade.

Method

C₃₆ Dimer acids (ca. 112 g, 0.2 mol) were taken in a 0.5 L four-necked flask equipped with a thermometer, a stirrer, and the Dean-Stark apparatus. The C₃₆ dimer acids were stirred and heated to about 5°C below the required temperature. Requisite amount of the polyamine was added within 2 min.

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The temperature rose to the required degree and was maintained within $\pm 1^\circ\text{C}$ by adjusting the electrical energy supplied using a energy regulator. Product samples were taken out at intervals and analyzed for acid and amine values using ASTM D 1980-61 and D 2074-62, respectively, by dissolving in a neutral mixture of ethanol and xylene (1 : 1, v/v). The reaction was continued until the acid value fell below 5. Thus, different experiments were carried out at temperatures ranging from 145°C to 190°C .

When the C_{36} diacid and the polyamine were reacted in the mole ratio of 1 : 1, the product was found to gel before it attained an acid value 5. Hence, in all the subsequent experiments the C_{36} diacid and the polyamine were reacted in the mol ratio of 1 : 1.2. The scheme for preparation of the reactive polyamide is shown in Figure 1.

RESULTS AND DISCUSSION

Polyamidation reactions, using the C_{36} dimer acids and different polyamines, namely, DETA and TETA in the mol ratio of 1 : 1.2, were performed at various temperatures in the range of 145°C to 190°C . The

acid and amine values of the intermittent products were determined. The reactions were followed from the fall in the acid and amine values with time at each temperature. Integral method of analysis was used to find the kinetics of the reactions. The reactions were assumed to follow an overall second-order kinetics that is first order with respect to the carboxyl group and amino group. The acid value (AV) and amine value (AmV) vs. reaction time data is tabulated in Tables I and II. Because the reactants were taken in the mole ratio of 1 : 1.2, the second order rate equation is written as¹³

$$\ln \frac{C_B}{MC_A} = (C_{B0} - C_{A0})kt \quad (1)$$

where C_{B0} and C_{A0} are the carboxyl and amine end groups present initially and C_B and C_A at time t (min), respectively, expressed as (eqs./ 10^6 g polymer), $M = (C_{B0}/C_{A0})$, k is the second-order rate constant expressed as (eqs./ 10^6 g polymer) $^{-1}$ (min) $^{-1}$, and t is the reaction time (min).

If AV_0 and AmV_0 (mg KOH/g polymer) are the acid and amine values at time $t = 0$, i.e., the time at which both the reactants are brought into contact, and AV and AmV are the acid and amine values at

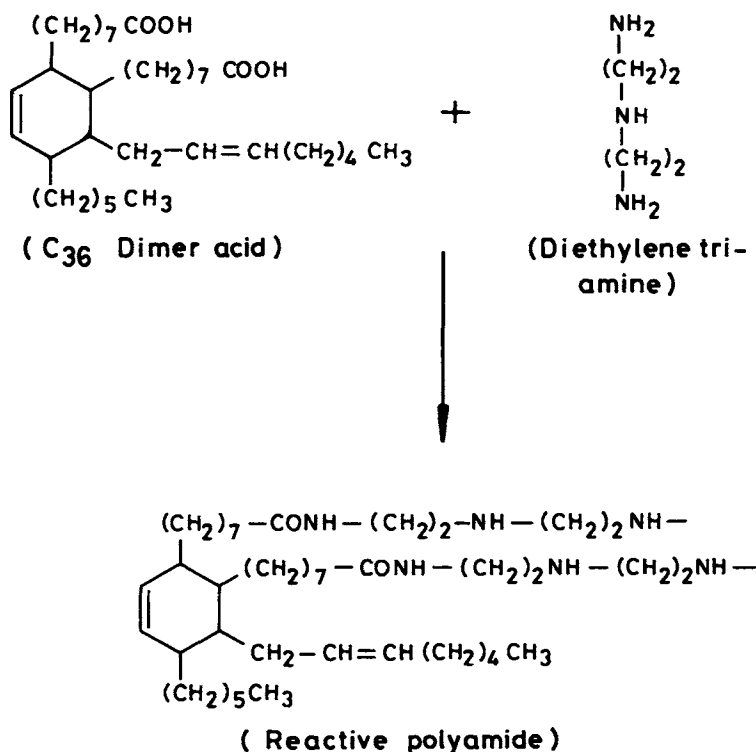


Figure 1 Reaction of C_{36} dimer acid and diethylenetriamine to get reactive polyamide.

Table I AV and AmV vs. Reaction Time at Various Temperatures for Polyamidation of C₃₆ Dimer Acids and DETA

| Exp. No. | Temp. (°C) | Reaction Time (min) | Av (mg KOH/g) | AmV (mg KOH/g) |
|----------|------------|---------------------|---------------|----------------|
| 1 | 2 | 3 | 4 | 5 |
| 1 | 145 | 0 | 160.5 | 294.6 |
| | | 15 | 79.6 | 192.8 |
| | | 45 | 52.0 | 176.3 |
| | | 80 | 28.3 | 155.0 |
| | | 140 | 16.3 | 152.3 |
| 2 | 155 | 180 | 6.8 | 126.6 |
| | | 0 | 160.5 | 294.6 |
| | | 10 | 94.7 | 185.3 |
| | | 30 | 55.8 | 170.3 |
| | | 45 | 33.6 | 133.9 |
| 3 | 165 | 70 | 22.5 | 128.2 |
| | | 120 | 9.1 | 122.2 |
| | | 0 | 160.5 | 294.6 |
| | | 5 | 83.7 | 161.8 |
| | | 20 | 42.9 | 146.5 |
| 4 | 175 | 60 | 15.3 | 118.9 |
| | | 120 | 3.9 | 115.8 |
| | | 0 | 160.5 | 294.6 |
| | | 5 | 70.1 | 162.4 |
| | | 35 | 21.9 | 135.2 |
| 5 | 190 | 60 | 7.2 | 125.3 |
| | | 80 | 4.0 | 121.3 |
| | | 0 | 160.5 | 294.6 |
| | | 5 | 47.4 | 156.6 |
| | | 15 | 25.7 | 138.7 |
| | | 25 | 11.7 | 134.7 |
| | | 35 | 7.2 | 127.4 |
| | | 45 | 3.1 | 123.6 |

Table II AV and AmV vs. Reaction Time at Various Temperatures for Polyamidation of C₃₆ Dimer Acids and TETA

| Exp. No. | Temp. (°C) | Reaction Time (min) | Av (mg KOH/g) | AmV (mg KOH/g) |
|----------|------------|---------------------|---------------|----------------|
| 1 | 2 | 3 | 4 | 5 |
| 1 | 145 | 0 | 150.9 | 366.0 |
| | | 10 | 83.4 | 229.4 |
| | | 30 | 42.6 | 137.3 |
| | | 70 | 19.6 | 122.5 |
| | | 100 | 12.8 | 119.5 |
| 2 | 155 | 0 | 150.9 | 366.0 |
| | | 5 | 82.6 | 221.4 |
| | | 20 | 50.9 | 185.6 |
| | | 40 | 31.5 | 172.3 |
| | | 60 | 18.8 | 155.1 |
| 3 | 160 | 120 | 4.4 | 124.1 |
| | | 0 | 150.9 | 366.0 |
| | | 5 | 69.3 | 190.0 |
| | | 20 | 39.2 | 174.2 |
| | | 40 | 20.5 | 162.7 |
| 4 | 175 | 70 | 8.2 | 152.8 |
| | | 90 | 4.9 | 148.2 |
| | | 0 | 150.9 | 366.0 |
| | | 5 | 51.5 | 155.6 |
| | | 20 | 26.6 | 140.2 |
| 5 | 190 | 40 | 11.4 | 131.3 |
| | | 60 | 5.1 | 127.5 |
| | | 0 | 150.9 | 366.0 |
| | | 5 | 40.7 | 139.2 |
| | | 20 | 15.3 | 125.9 |
| | | 32 | 5.7 | 122.5 |
| | | 45 | 3.8 | 118.4 |

time t (min), respectively, then the concentrations can be expressed as

$$C_{AO} = \frac{10^6(AV_0)}{56100}, \quad C_A = \frac{10^6(AV)}{56100}$$

$$C_{BO} = \frac{10^6(AmV_0)}{56100}, \quad C_B = \frac{10^6(AmV)}{56100}$$

Hence, eq. (1) can be written as

$$\ln \frac{AmV}{AV} = \frac{(AmV_0 - AV_0)}{0.0561} kt + \ln \frac{AmV_0}{AV_0} \quad (2)$$

Using eq. (2), a plot of $\ln (AmV/AV)$ vs. time was drawn and was found to fit the equation well at all

Table III Reaction Rate Constant at Various Temperatures for the Polyamidation Reactions

| Reaction | Temp. (°C) | Reaction Rate Constant $k \times 10^3$ (eqs./10 ⁶ g polymer) ⁻¹ (min ⁻¹) |
|------------------------------------|------------|--|
| C ₃₆ Dimer Acids + DETA | 145 | 0.0050 |
| | 155 | 0.0071 |
| | 165 | 0.0097 |
| | 175 | 0.0147 |
| | 190 | 0.0271 |
| C ₃₆ Dimer Acids + TETA | 145 | 0.0036 |
| | 155 | 0.0053 |
| | 160 | 0.0068 |
| | 175 | 0.0101 |
| | 190 | 0.0154 |

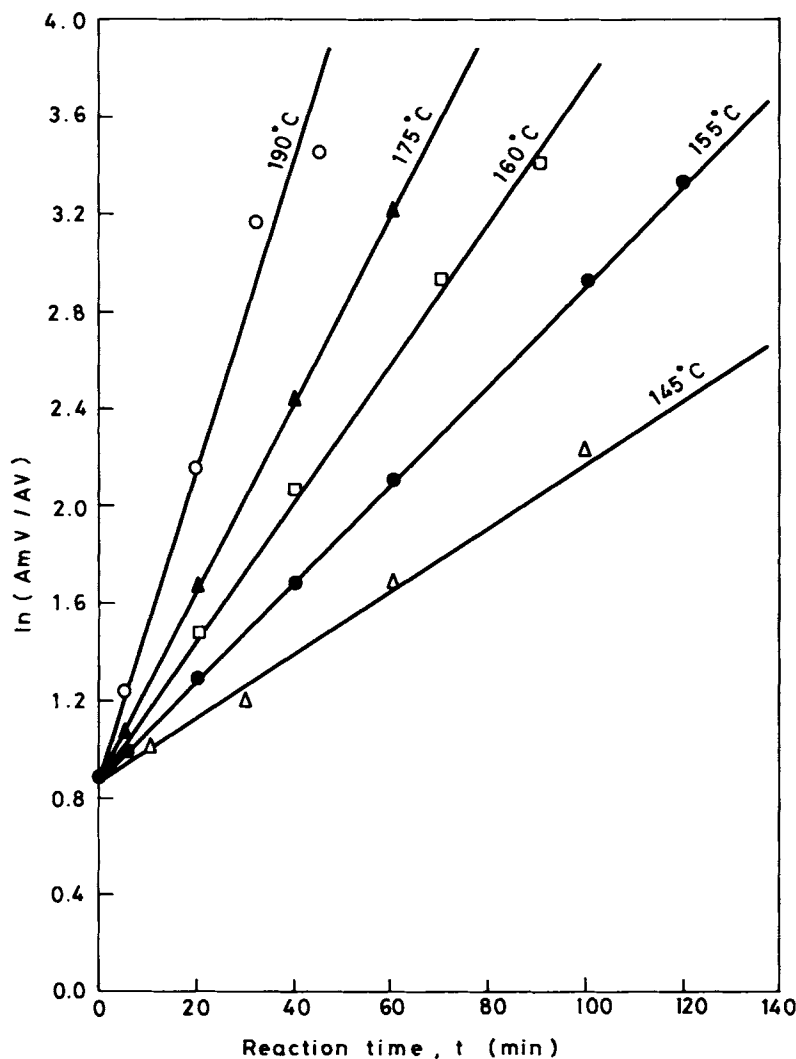


Figure 2 Plot of $\ln (AmV / AV)$ with time at different temperatures for polyamidation of C_{36} diacids and DETA.

the temperatures studied as shown in Figures 2 and 3. Linear regression analyses of the $\ln (AmV / AV)$ vs. reaction time data showed that the regression coefficient had a value of above 0.99 in each case. This also confirmed that the polyamidation reaction, indeed, follows the second-order kinetics. The re-

action rate constants, k , found from the linear regression analyses are tabulated in Table III.

The data of reaction rate constant (k) vs. temperature were found to fit the Arrhenius equation,

$$k = k_0 e^{-E/RT}$$

Table IV Activation Energies and Frequency Factors for the Different Polyamidation Reactions

| Property | Polyamidation of C_{36} Dimer Acids and DETA | Polyamidation of C_{36} Dimer Acids and TETA |
|---|--|--|
| Activation Energy (kcal/g mol) | 14.4 | 12.3 |
| Frequency factor (eqs./ 10^6 g polymer) $^{-1}$ (min) $^{-1}$ | 156.5 | 9.5 |

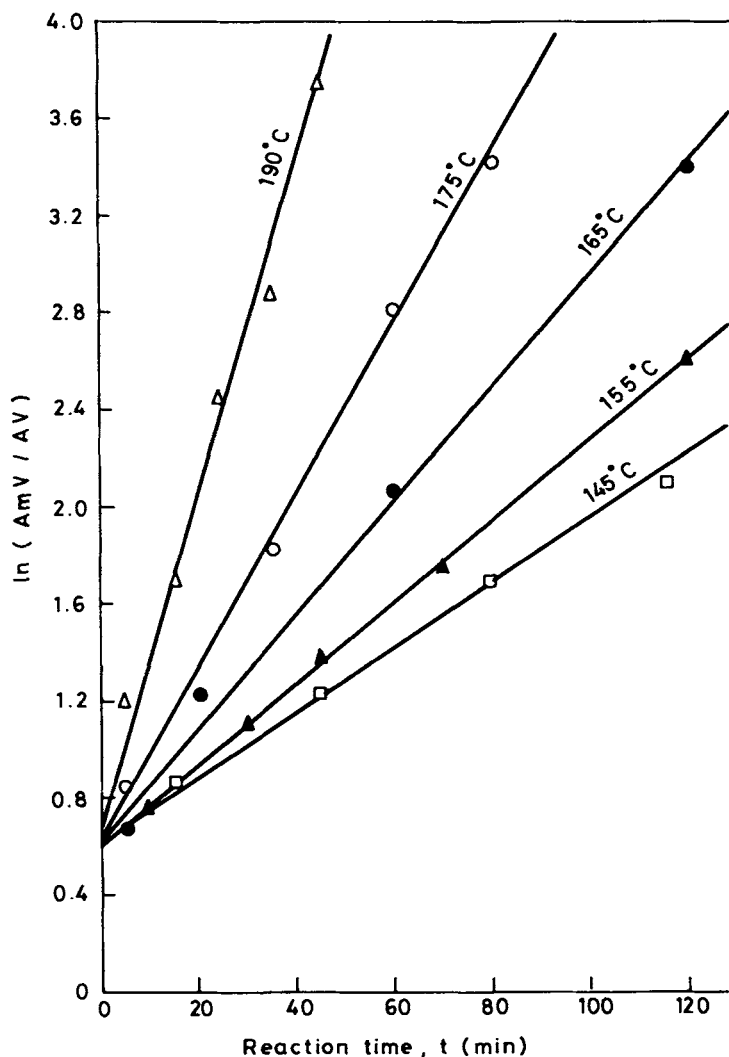


Figure 3 Plot of $\ln (AmV / AV)$ with time at different temperatures for polyamidation of C_{36} diacids and TETA.

quite well for the polyamidation reaction (Fig. 4). The activation energy and frequency factor were calculated by linear regression analyses of the $\ln k$ vs. $1/T$ data of Figure 4 and are tabulated in Table IV. Using the activation energy and the frequency factor in eq. (2), generalized design equations were found for the reactions. These generalized design equations are:

$$\ln \frac{AmV}{AV} = \frac{(AmV_0 - AV_0) \times 156.5 \times e^{(-14400/1.987T)}}{(0.0561)} t + \ln \frac{AmV_0}{AV_0} \quad (3)$$

for the polyamidation of C_{36} diacid and DETA and

$$\ln \frac{AmV}{AV} = \frac{(AmV_0 - AV_0) \times 9.5 \times e^{(-12300/1.987T)}}{(0.0561)} + \ln \frac{AmV_0}{AV_0} \quad (4)$$

for polyamidation of C_{36} diacid and TETA.

The values of $\ln (AmV / AV)$ calculated using eqs. (3) and (4) were plotted against the observed $\ln (AmV / AV)$ as shown in Figures 5 and 6. The absolute percent deviation in the $\ln (AmV / AV)$ calculated using the design equations and the observed $\ln (AmV / AV)$ at all the temperatures was below 6% in the case of both the polyamidation reactions.

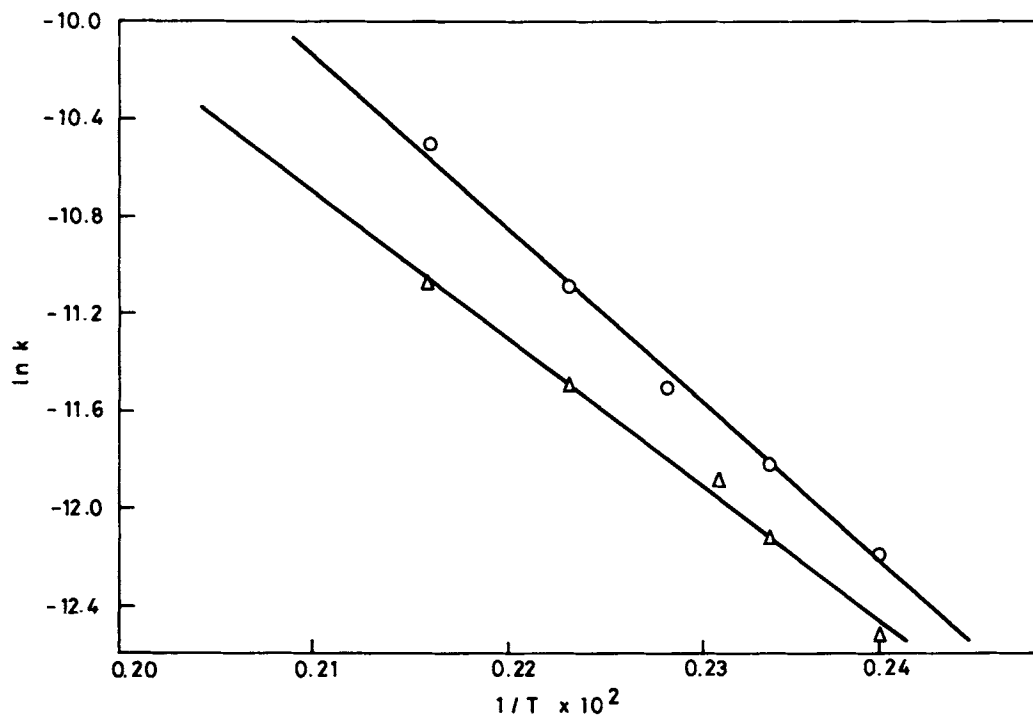


Figure 4 Temperature dependency of reaction rate constant: O, Polyamidation of C₃₆ diacids and DETA; Δ, Polyamidation of C₃₆ diacids and TETA.

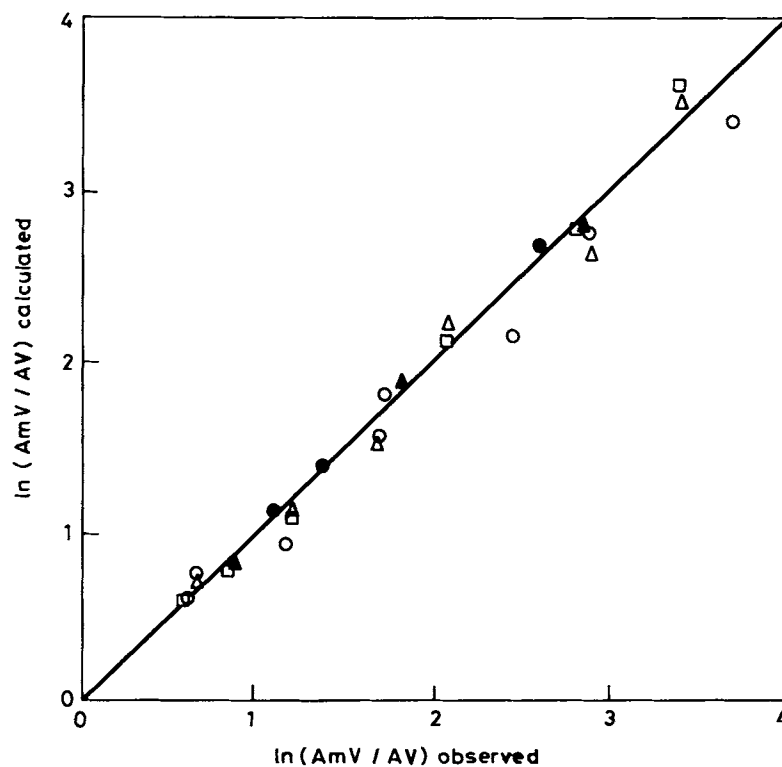


Figure 5 Plot of ln (AmV / AV) observed vs. ln (AmV / AV) calculated for polyamidation of C₃₆ diacids and DETA O, 190°C; Δ, 175°C; □, 160°C, ●, 155°C; ▲, 145°C.

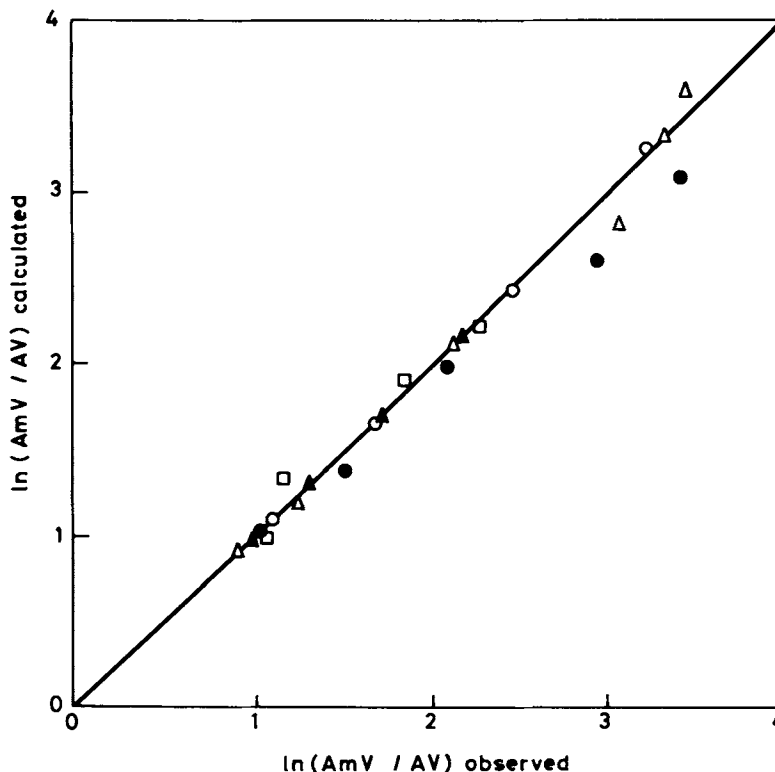
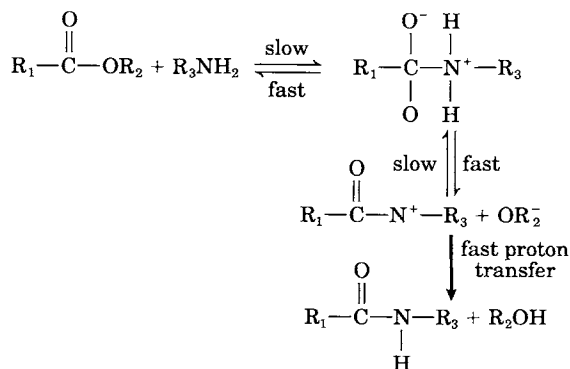


Figure 6 Plot of $\ln (AmV / AV)$ observed vs. $\ln (AmV / AV)$ calculated for polyamidation of C_{36} diacids with TETA Δ , $190^{\circ}C$; \circ , $175^{\circ}C$; \bullet , $165^{\circ}C$; \blacktriangle , $155^{\circ}C$; \square , $145^{\circ}C$.

CONCLUSIONS

Studying the kinetics of a chemical reaction helps in arriving at the optimum reaction parameters required to get a desired conversion of the reactants and this, in turn, helps in the design of a reactor. The literature on kinetics of polyamidation reactions involving diamines and dicarboxylic acids shows that these reactions follow second-order kinetics and in some cases third-order kinetics at conversion above 90%.⁴ The activation energies^{4,14} of these reactions are ca. 15 kcal/g mol. The mechanism for the second order polyamidation reaction is similar to that of carboxylic esterification and is represented below.¹⁴



where R_1 and R_3 are alkyl groups and R_2 represents H or alkyl groups.

In the present study, the polyamidation of C_{36} diacid and DETA and TETA were found to follow second-order kinetics. Their activation energies are 14.4 kcal/g mol and 12.3 kcal/g mol, respectively. These results are in agreement with the results obtained for different polyamidation reactions.

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