

Kinetics of Reaction of Ethylenediamine and Dimeric Fatty Acids*

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Synopsis

Kinetic studies were carried out on the reaction between ethylenediamine and dimeric fatty acids in melt phase. The reaction was performed at 124, 130, 145, 160, 174, and 190°C and followed by determining the acid value of the product. The polyamidation reaction was found to be of overall second order with an activation energy of 18.2 kcal/g mol up to 90% conversion and of overall third order with an activation energy of 16.4 kcal/g mol above 90% conversion.

INTRODUCTION

Fatty polyamides are condensation products of di- and polyfunctional amines and di- and polybasic fatty acids. The latter are obtained by the polymerization of unsaturated fatty acids or their esters. Fatty polyamides find varied uses, e.g., thermoplastics, thermosetting adhesives, surface coatings, rotogravure, and flexographic printing inks. Much of the literature on fatty polyamide preparation is patented and no work has been reported on the kinetics of this reaction except for products¹ such as nylon 6 and nylon 6,6. Hence, the present work on kinetics of the polyamidation reaction in melt phase for preparing nonreactive polyamides has been carried out.

EXPERIMENTAL

Materials. Dimeric fatty acids (Empol 1010 grade from Emery Industries Inc., U.S.A.) were 97% pure and had iodine value below 20. Ethylenediamine was laboratory reagent grade having purity of above 98% as determined by titration with standard acid. All other materials were reagent grade.

Method. A 1-L round bottom flask, equipped with stirrer, nitrogen inlet tube, thermowell, Dean-Stark apparatus and addition funnel, was charged with known weight (ca. 300 g) of dimeric fatty acids and heated in an isomantle. An equivalent molar quantity of ethylenediamine was added within 2 min, and the heating was regulated to get the desired temperature within 10 min. The polyamidation reaction was carried out at six different temperatures in the range of 120–190°C. In this temperature range the reaction mass

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remained in molten state. The water generated during the reaction was swept out of the system by nitrogen bubbled through the reacting melt at a sweep rate of ca. 12 mL/min and collected in the Dean-Stark apparatus. This helped the reaction to go in the forward direction. The samples were taken out at intervals and analyzed for acid value. A few samples were also analyzed for amine value. The acid and amine values were determined as per ASTM D-1980-67 and ASTM D-2074-62T using a neutral solution (1:1, v/v) of *n*-butanol and xylene for dissolving the samples.

RESULTS AND DISCUSSION

The polyamidation reaction in melt phase was carried out at 124, 130, 145, 160, 174, and 190°C and was followed by determining the acid values of the product at each temperature. A few of the products were also analyzed for amine value. It was found that both the values were almost equal for different products which shows that the reaction could be followed by the fall in either acid or amine value. The variation in acid values with reaction time is tabulated in Table I. The integral method of analysis was used for studying the kinetics of the reaction. Based on the data available in the literature on kinetics of other polyamidation reactions¹⁻⁵ and also by observing the nonlinear trend in the fall of acid value with time, it was assumed that the acid value-time relation would characterize an overall second-order reaction which is first order with respect to both the carboxyl and amine group concentration.

TABLE I
Variation of Acid Value with Reaction Time at Various Temperatures

Temp (°C)	Reaction time (min)	Acid value (mg KOH/g polymer)	Temp (°C)	Reaction time (min)	Acid value (mg KOH/g polymer)
124	2	160.4	160	8	109.1
	12	150.8		18	58.5
	32	127.3		48	31.1
	92	96.7		88	19.4
	152	83.3		138	14.4
	212	72.4		170	12.7
130	2	163.9	174	208	11.2
	65	82.6		2	142.0
	125	65.7		18	50.4
	180	51.6		45	24.5
	240	43.3		60	19.2
145	4	152.5	190	93	15.2
	10	115.5		121	13.2
	20	94.2		155	11.7
	30	79.8		15	58.5
	60	58.8		25	35.2
	120	31.5		50	18.7
	180	21.5		70	14.5
	220	19.4		92	12.5
	265	16.7		135	9.9
	300	16.1			
	350	14.8			

Since equivalent amounts of the acid and amine were taken initially and since the reaction is homogeneous, the following equation is used for the second-order kinetics:

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \quad (1)$$

where C_{A0} and C_A are the carboxyl end group contents present initially and at time t (min), respectively, expressed as eqs/10⁶ g polymer, k is the second-order rate constant expressed as (eqs/10⁶ g polymer)⁻¹ min⁻¹, and t is the reaction time (min).

If $(AV)_0$ and AV are the acid values (mg KOH/g polymer) at time $t = 0$, i.e., the time at which both the reactants are brought into contact, and at time t (min), respectively, then C_{A0} and C_A can be expressed as

$$C_{A0} = \frac{10^6(AV)_0}{56,100}$$

and

$$C_A = \frac{10^6(AV)}{56,100}$$

Hence eq. (1) can be written as

$$\frac{1}{AV} - \frac{1}{(AV)_0} = \frac{k}{(0.0561)}t \quad (2)$$

Using eq. (2), a plot of $1/AV$ vs. time was drawn and was found to fit the equation quite well up to about 90% conversion at all the temperatures studied as shown in Figure 1. This shows that the polyamidation reaction follows second-order kinetics up to 90% conversion. The second-order kinetic plots show a downward curvature above 90% conversion, indicating the possibility of an increase in the order of the reaction. It has also been reported in the literature² that the results of the polyamidation reaction carried out under conditions in which the end group concentrations are relatively low (e.g., conversions above 90%) indicate that a carboxyl-catalyzed third-order reaction assumes increasing importance and becomes predominant. Hence it was assumed that the reaction would follow an overall third-order kinetics above 90% conversion, which is second order with respect to the acid group concentration and first order with respect to the amino group concentration. Since the carboxyl and amino group concentrations are equal, the integrated rate equation for this reaction can be written as

$$\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 2k't' \quad (3)$$

where C_{A0} = acid group concentration at 90% conversion (i.e., at time t_n taken from Fig. 1) expressed as eqs/10⁶ g polymer, C_A = acid group concentration at

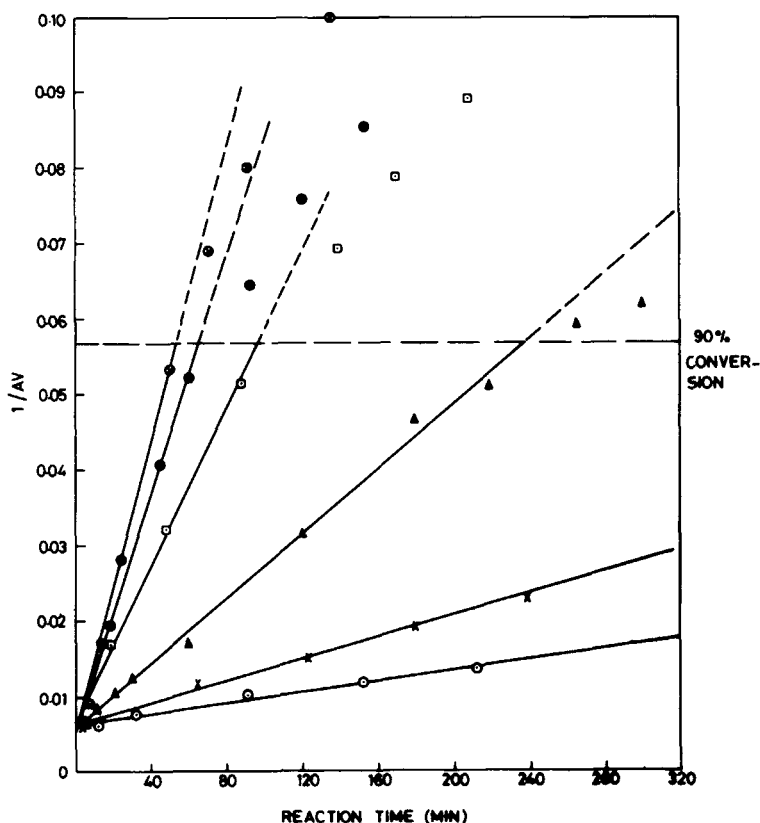


Fig. 1. Change in $1/AV$ with time at various temperatures: (●) 190°C ; (●) 174°C ; (□) 160°C ; (▲) 145°C ; (×) 130°C ; (○) 124°C .

any time t' above 90% conversion, expressed as eqs/ 10^6 g polymer, $t' = t - t_n$, and k' = third-order rate constant expressed as (eqs/ 10^6 g polymer) $^{-2}$ min $^{-1}$.

If $(AV)_0$ and AV are the acid values at time t_n and at time t' (min), respectively, then eq. (3) in terms of acid values can be written as

$$\frac{1}{(AV)^2} = \frac{2k't'}{(0.0561)^2} + \frac{1}{(AV)_0^2} \quad (4)$$

A plot of $1/(AV)^2$ vs. reaction time t' was drawn as shown in Figure 2 and was found to fit eq. (4) for the four different temperatures studied.

The second- and third-order reaction rate constants calculated by the least square analysis of the data of Figures 1 and 2, respectively, are given in Table II. These rate constants were found to fit the Arrhenius equation well as shown in Figure 3. The Arrhenius equation is

$$k = k_0 e^{-E/RT} \quad (5)$$

where k = reaction rate constant [(concn) $^{1-n}$ (time) $^{-1}$], E = activation energy

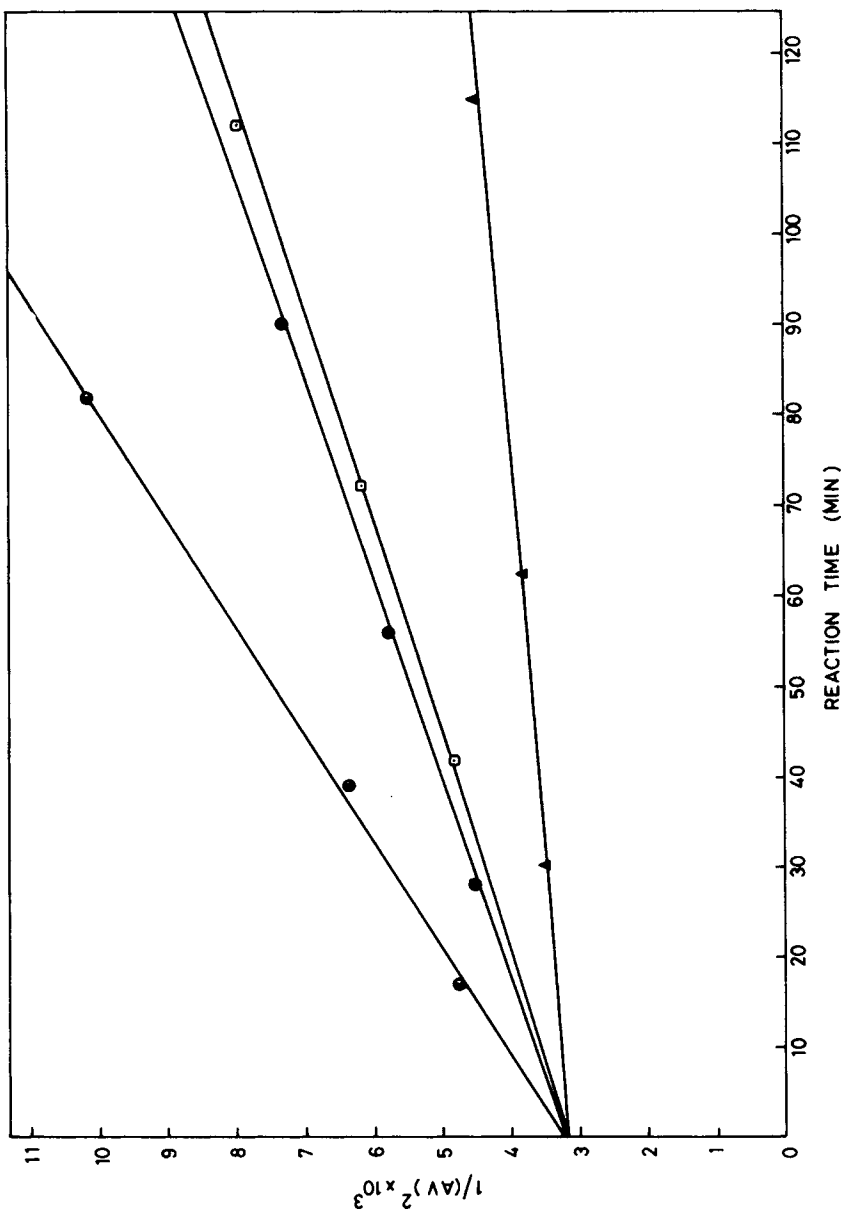


Fig. 2. Change in $1/(AV)^2$ with time at various temperatures above 90% conversion: (◻) 190°C; (●) 174°C; (◻) 160°C; (▲) 145°C.

TABLE II
Reaction Rate Constants at Various Temperatures

Reaction temp (°C)	Second order rate constant $k \times 10^5$ [(eq/10 ⁶ g polymer) ⁻¹ min ⁻¹]	Third order rate constant $k' \times 10^7$ [(eq/10 ⁶ g polymer) ⁻² min ⁻¹]
124	0.2196	—
130	0.4110	—
145	1.1980	0.1697
160	2.9240	0.6648
174	4.3860	0.7284
190	5.5010	1.3336

(kcal/g mol), R = gas constant, T = absolute temperature (K), k_0 = frequency factor [(concn)¹⁻ⁿ(time)⁻¹], and n = order of reaction.

The activation energy and frequency factor for the second- and third-order reactions were calculated from the least square analysis of the data of Figure 3 and were found to be 18.2 kcal/g mol and 527.3 (eqs/10⁶ g polymer)⁻¹ min⁻¹ for the second-order reaction and 16.4 kcal/g mol and 7.9 (eqs/10⁶ g polymer)⁻² min⁻¹ for the third-order reaction. Using these values of activation energy and frequency factor, generalized design equations for the second-

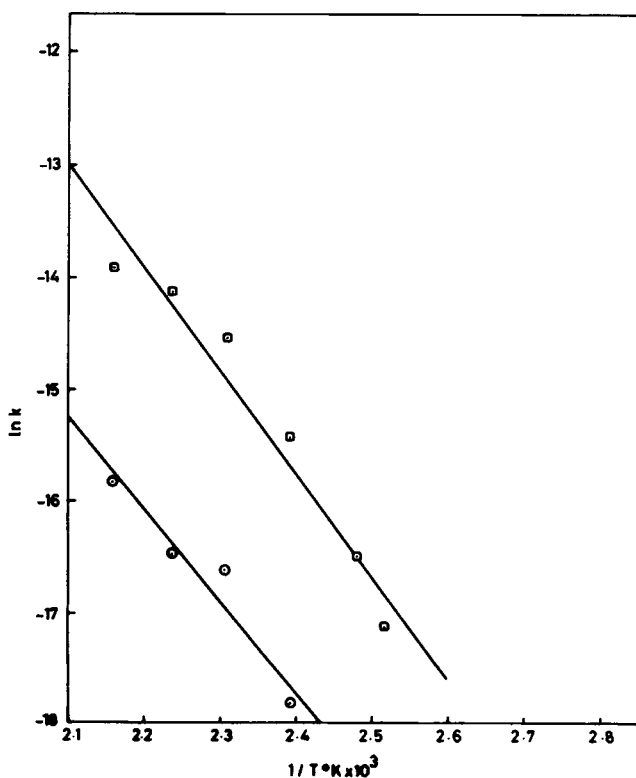


Fig. 3. Temperature dependency of reaction rate constant; (□) up to 90% conversion; (⊙) above 90% conversion.

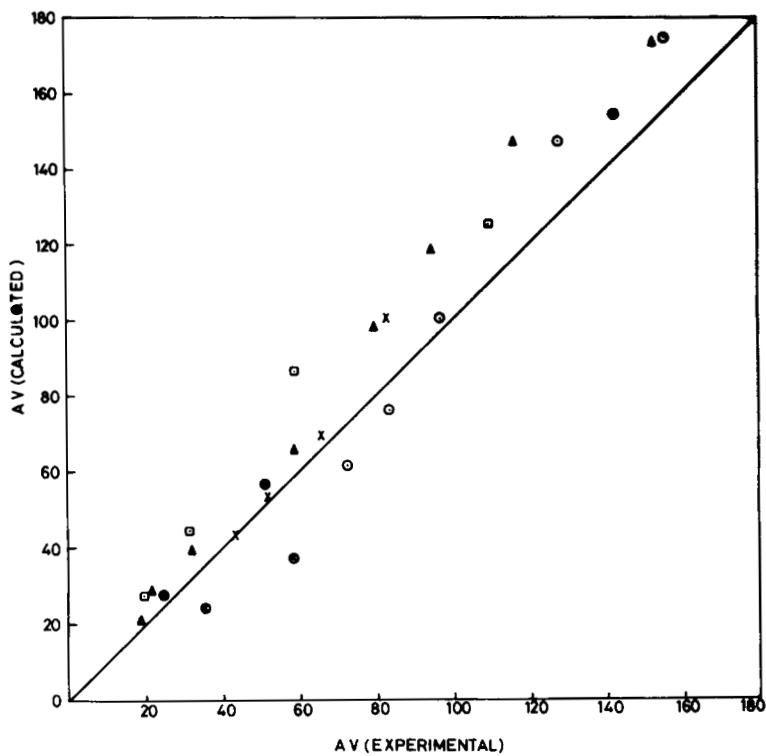


Fig. 4. Plot of AV (calcd) vs. AV (exptl) up to 90% conversion at various temperatures: (⊗) 190°C; (●) 174°C; (◻) 160°C; (▲) 145°C; (×) 130°C; (⊙) 124°C.

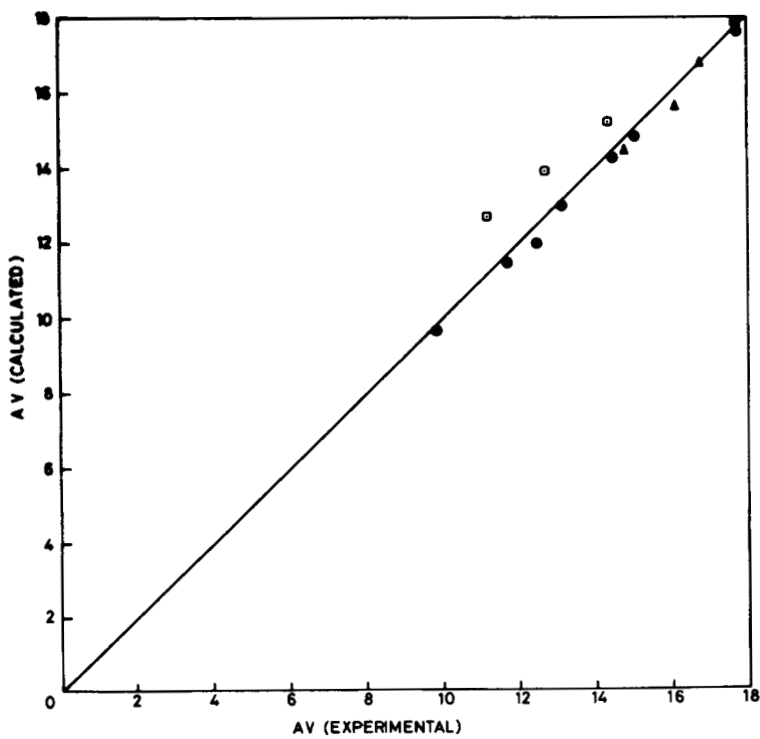


Fig. 5. Plot of AV (calcd) vs. AV (exptl) above 90% conversion at various temperatures: (⊗) 190°C; (●) 174°C; (◻) 160°C; (▲) 145°C.

and third-order reactions were deduced from eqs. (2) and (4), respectively. The acid values calculated using these design equations were plotted against experimental acid values at different temperatures as shown in Figures 4 and 5. It was found that the absolute percentage deviation between the experimental and calculated acid values was ca. 15% for the second-order reaction and ca. 4% for the third-order reaction.

CONCLUSIONS

The melt phase polyamidation reaction involving dimeric fatty acids and ethylenediamine follows an overall second-order kinetics up to 90% conversion with an activation energy of 18.2 kcal/g mol and third-order kinetics above 90% conversion with an activation energy of 16.4 kcal/g mol. It appears that the increase in the order of the polyamidation reaction above 90% conversion is because of the carboxyl catalyzed third-order reaction becoming predominant. These results are in agreement with those reported in the literature^{1,2} for other polyamidation reactions.

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