

Kinetics of Reaction of C₃₆ Dimeric Fatty Acids and Ethylenediamine in Solution*

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SYNOPSIS

Kinetic studies were carried out on the reaction between ethylenediamine and C₃₆ dimeric fatty acids using benzyl alcohol as solvent. The reaction was performed at four different temperatures in the range of 160–190°C, and the products were analyzed for acid and amine values intermittently to follow the reaction. The fall in both the values was almost the same throughout the reaction. The kinetics was determined from the fall in acid value, and the reaction was found to be of overall third order and had an activation energy of 30.7 kcal mol⁻¹ (128.5 kJ mol⁻¹).

INTRODUCTION

Fatty polyamides are condensation products of di- and polyfunctional amines and di- and polybasic fatty acids. They are used in thermoplastic and thermosetting adhesives, surface coatings, and rotogravure and flexographic printing inks.¹ Studies of the polycondensation of amine-carboxylic acid systems have been carried out on amino acids and salts of diamines and dicarboxylic acids in solution, in melts, and in the solid state.² Korshak et al.³ studied linear polyamides formation in solution using the balanced salt of hexamethylenediamine and sebacic acid in *m*-cresol over the temperature range of 140–185°C, Zhubanov et al.⁴ studied the condensation in *m*-cresol of *p*- and *m*-xylenediamine with different dicarboxylic acids as well as the self-condensation of aminoheptanoic and aminoundecanoic acids. Literature on kinetics of polyamidation in melt phase and in solid state of nylon 6 and nylon 6.6 is available,² but literature on kinetics of preparation of fatty polyamides is not available. Recently, kinetics of reaction of ethylenediamine and C₃₆ dimeric fatty acids in melt phase has been reported by us.⁵

In the present work kinetics of polyamidation reaction of ethylenediamine and C₃₆ dimeric fatty acids using benzyl alcohol as solvent is reported.

EXPERIMENTAL

Materials

Dimeric fatty acids (Empol 1010 grade from Emery Industries Inc., U.S.A.) were 97% pure and had acid value of 196 and iodine value of 18. Ethylenediamine was laboratory reagent grade having purity above 98% as determined by titration with standard acid. All other materials were reagent grade.

Method

A reaction mixture consisting of ca. 56 g (0.1 mol) of the dimeric fatty acids and 50 mL of benzyl alcohol were charged into a 0.5-L round-bottomed flask equipped with a stirrer, nitrogen inlet tube, thermowell, Dean-Stark arrangement, and addition funnel. The mixture was stirred and heated in an isomantle to the desired temperature. An equivalent molar quantity of 70% aqueous ethylenediamine was added within 2 min, and the heating was regulated to get the desired temperature within 5–10 min. The water generated during the reaction was collected in the Dean-Stark apparatus. The product samples

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were taken out intermittently and analyzed for acid value and amine value as per ASTM D-1980-67 and ASTM D-2074-62 T, respectively, using a neutral solution of ethanol and toluene (1 : 1, v/v) for dissolving the samples. The polyamidation reaction was carried out at four temperatures in the range of 160–190°C.

RESULTS AND DISCUSSION

The polyamidation reaction using benzyl alcohol as solvent was carried out at 160, 170, 180, and 190°C and was followed by determining the acid and amine values of the product at each temperature. The product acid values were found to be almost equal to their amine values, indicating nonformation of side products, and the reaction could be followed by the fall in either acid value or amine value of the product. The variation in acid value with reaction time is shown in Table I. The integral method of analysis was used to study the kinetics. The acid value versus reaction time data did not fit an overall

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

Temp. (°C)	Reaction Time (h)	Acid Value (mg KOH/g polymer)
160	0.25	64.5
	0.5	51.8
	1.0	40.3
	2.0	30.3
	3.75	22.7
170	0.08	87.0
	0.25	55.9
	0.50	44.1
	1.00	30.6
	2.00	21.1
180	0.08	65.0
	0.25	38.0
	0.50	28.9
	1.00	21.1
	2.00	14.9
190	0.08	12.3
	0.08	48.0
	0.25	28.6
	0.50	20.2
	1.00	14.3
	2.00	9.9

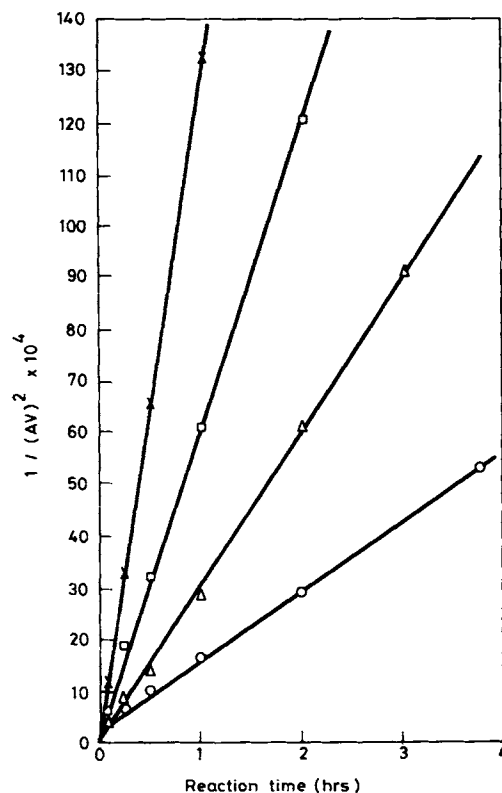


Figure 1 Change in $1/(AV)^2 \times 10^4$ with reaction time at various temperatures: \times 190°C; \square 180°C; \triangle 170°C; \circ 160°C.

second-order kinetics. Hence it was assumed that the polyamidation reaction would follow a carboxyl-catalyzed overall third-order kinetics that is second order with respect to the carboxyl group concentration and first order with respect to the amino group concentration. Since the reaction is homogeneous and the carboxyl and amino group concentrations are equal, the integrated rate equation for the reaction can be written as

$$\frac{1}{C_A} - \frac{1}{C_{AO}} = 2kt \quad (1)$$

where C_{AO} and C_A are the carboxyl end group concentrations present initially and at time t (h), respectively, expressed as eq/10⁶ g polymer, k is the third-order rate constant expressed as (eq/10⁶ g polymer)⁻² (h⁻¹), and t is the reaction time (h).

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 (h), respectively, then C_{AO} and C_A can be expressed

Table II Third-Order Reaction Rate Constants at Various Temperatures

Reaction Temp. (°C)	Rate Constant $k \times 10^{12}$ (equiv. ⁻¹ L) ² s ⁻¹
160	11.6
170	25.8
180	51.3
190	119.0

as

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

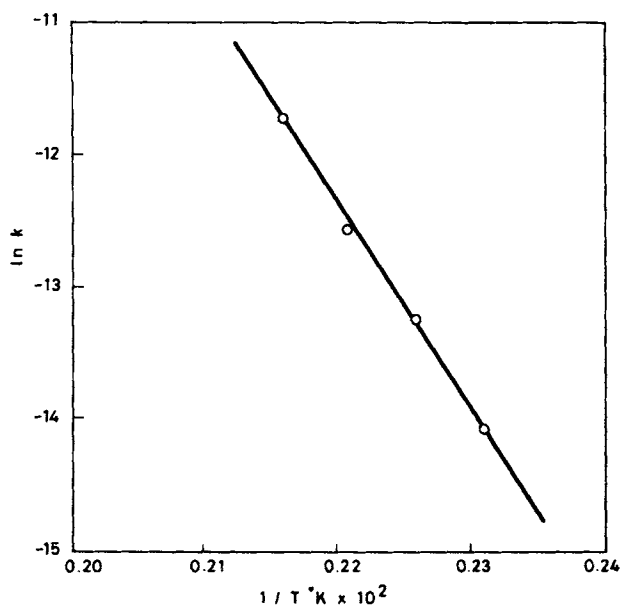
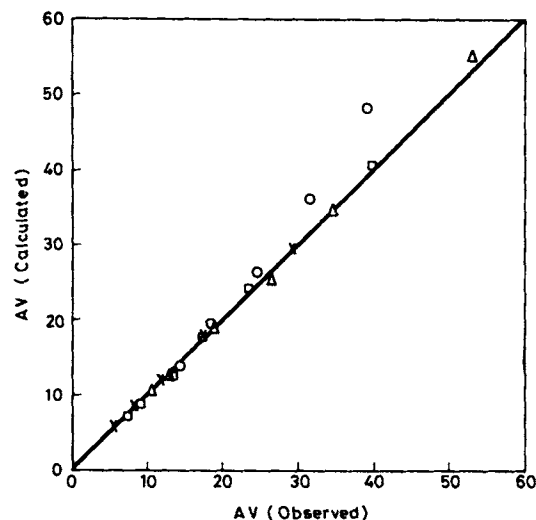
and

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

Hence Eq. (1) can be written as

$$\frac{1}{(AV)^2} - \frac{1}{(AV)_0^2} = \frac{2kt}{(0.0561)^2} \quad (2)$$

As per Eq. (2) a plot of $1/(AV)^2$ versus reaction time should be linear for third-order kinetics. The

**Figure 2** Temperature dependency of reaction rate constant.**Figure 3** Plot of AV (calculated) vs. AV (experimental) at different temperatures (°C): × 190°C; □ 180°C; △ 170°C; ○ 160°C.

plots of $1/(AV)^2$ versus reaction time in Figure 1 were found to be linear. This indicates that the reaction followed third-order kinetics at all the temperatures. The third-order reaction rate constants calculated by the least-square analysis of the data of Figure 1 are given in Table II. These rate constants were found to fit the Arrhenius equation well, as shown in Figure 2. The activation energy and the frequency factor for the reaction were calculated from the least-square analysis of the data in Figure 2 and were found to be $30.7 \text{ kcal mol}^{-1}$ ($128.5 \text{ kJ mol}^{-1}$) and $34.6 \times 10^{-3} \text{ (equiv.}^{-1} \text{ L s)}^2 \text{ s}^{-1}$, respectively. Using these values of the activation energy and frequency factor, a generalized design equation for the third-order reaction was deduced from Eq. (2). The acid values calculated at different reaction times using the design equation were plotted against the experimental acid values at different temperatures, as shown in Figure 3. The absolute percent deviation between the experimental and calculated acid values was ca. 4%.

The melt phase polyamidation of dimeric fatty acids and ethylenediamine⁵ was found to follow second-order kinetics up to 90% conversion with an activation energy of $18.2 \text{ kcal mol}^{-1}$ (76.2 kJ mol^{-1}) and third-order kinetics above 90% conversion with an activation energy of $16.4 \text{ kcal mol}^{-1}$ (68.7 kJ mol^{-1}). In the present studies the reaction using benzyl alcohol as solvent was found to follow third-order kinetics and had an activation energy of $30.7 \text{ kcal mol}^{-1}$ ($128.5 \text{ kJ mol}^{-1}$).

CONCLUSIONS

The polyamidation reaction between dimeric fatty acids and ethylenediamine in solution using benzyl alcohol as solvent follows an overall third-order kinetics with an activation energy of $30.7 \text{ kcal mol}^{-1}$ ($128.5 \text{ kJ mol}^{-1}$).

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