Kinetics of Polymerization of Dimer Fatty Acids with Ethylenediamine

Javad Heidarian, Nayef Mohd Ghasem, Wan Mohd Ashri Wan Daud

Department of Chemical Engineering, University of Malaya, 50603, Kuala Lumpur, Malaysia

ABSTRACT: A generally applicable stoichiometric and kinetic model was developed for the polymerization of dimer fatty acids with ethylenediamine. The rate equations were second-order before 90% conversion and were used between 405 and 475 K. The parameters of the rate equations were determined with nonlinear regression analysis. A comparison of the model predictions and the experimental data showed that the approach was useful in predicting the polymerizatio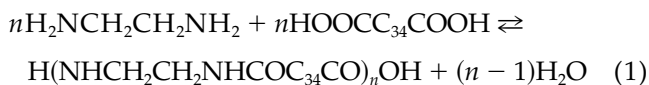n kinetics. The equilibrium constant changed from 3.175 to 7.311. The frequency factor and activation energy for the forward rate constant before 90% conversion were 2,716,894 kg mol^{-1} min^{-1} and 66.7 kJ mol^{-1}, respectively. The equilibrium constant was independent of the temperature at frequency factor and activation energy values of 74.4 and 9.7 kJ mol^{-1}, respectively. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2504–2513, 2004

Key words: polyamides; kinetics (polym.); modeling

INTRODUCTION

Dimer fatty acids have traditionally been used to synthesize and formulate hot-melt adhesives, flexographic inks, functional coatings, and other engineering materials.[1]

Equation (1) shows the polymerization reaction between dimer fatty acids and ethylenediamine:

$$n\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 + n\text{HOOCC}_{34}\text{COOH} \rightleftarrows$$

$$\text{H}(\text{NHCH}_2\text{CH}_2\text{NHCOC}_{34}\text{CO})_n\text{OH} + (n-1)\text{H}_2\text{O} \quad (1)$$

In industry, the water produced during the reaction should be purged to minimize the reverse reaction. The evaporation of ethylenediamine during the reaction is another important factor that needs to be considered because if the evaporation becomes high, the loss of ethylenediamine will cause an imbalance between the acid and amine values, and this will affect the final product. To obtain the reverse rate constant and the amount of evaporation with the temperature and time, we need an appropriate model.

Most of the publications on fatty polyamide preparation are patents, and no substantial work has been reported on the modeling of the kinetics of this reaction, except for products such as nylon 6 and nylon 66.[2] Vijay et al.[3] studied the kinetics of the reaction between ethylenediamine and dimeric fatty acids in the melt phase in the temperature range of 399–465 K and found that the reaction was second-order with an activation energy of 76.44 kJ mol^{-1} for conversions of up to 90%. For higher conversions, the reaction was third-order overall with an activation energy of 68.88 kJ mol^{-1}.

In another work, Vijay et al.[4] carried out a kinetic study on the reaction between C$_{36}$ dimer acids and diethylenetriamine and triethylenetetramine in the temperature range of 420–465 K and found that the reactions overall followed second-order kinetics and had activation energies of 60.8 and 51.7 kJ mol^{-1}, respectively. These polyamides are known as reactive polyamides because they can be crosslinked with other resins such as epoxy resins and they are not linear.

Sumathi et al.[5] conducted kinetic studies on the reaction between ethylenediamine and C$_{36}$ dimeric fatty acids with benzyl alcohol as a solvent. The reaction was performed at temperatures between 435 and 465 K, and the kinetics were determined from the change in the acid value. The reaction was found to be third-order overall and had an activation energy of 128.9 kJ mol^{-1}. For reverse reaction and equilibrium constants, there are no published literature values available. In the aforementioned publication, nitrogen bubbling inside the reaction mass was applied to remove the water produced, and so the reaction could be considered irreversible.

In this work, the kinetics of the polyamidation reaction of ethylenediamine and dimer fatty acid are modeled with MATLAB, EXCEL, and EASY-FIT software, and the generated results are compared with the experimental data obtained. The reverse reaction and evaporation of water and amine are also examined.
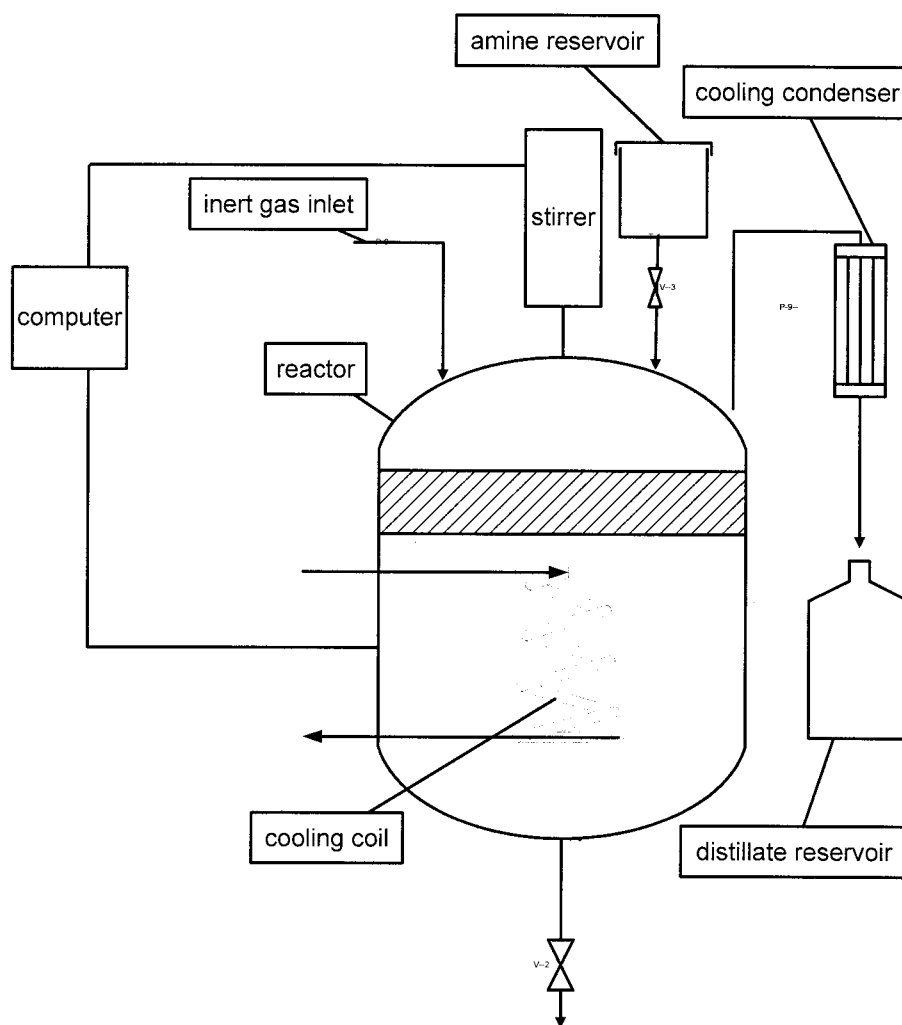
Figure 1 Diagram of the melt polymerization of fatty polyamides.

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TABLE I
Amine Values with Time for Different Temperatures

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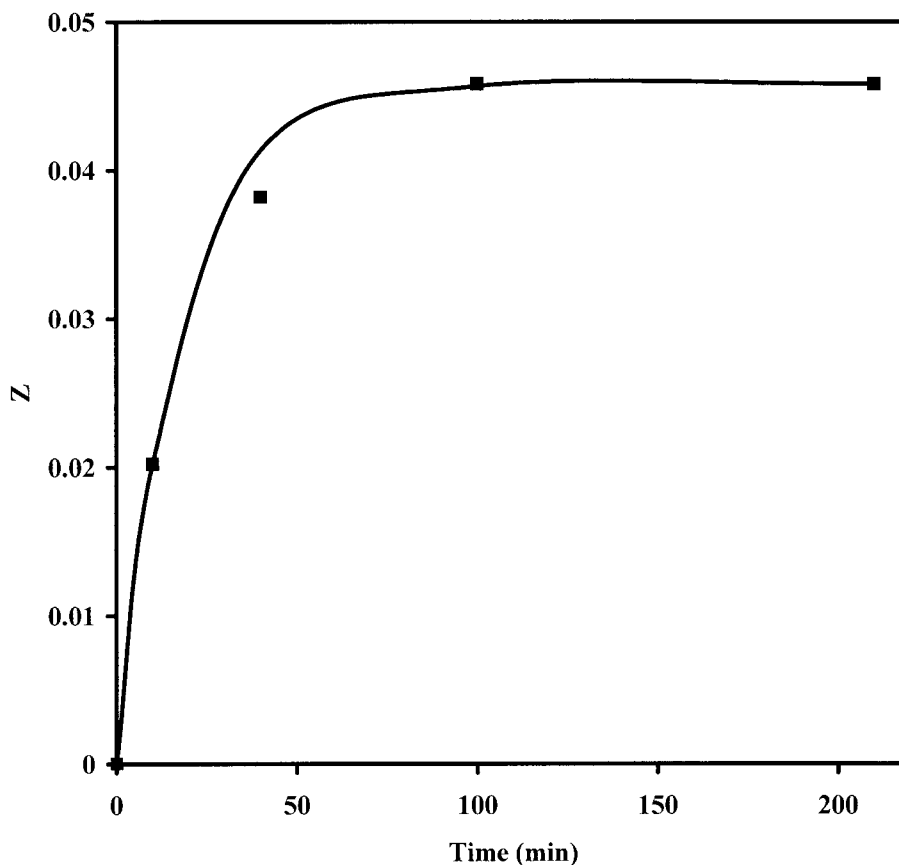| T (K)	Reaction time (min)	Amine value (mg of KOH g of polymer^{-1})	T (K)	Reaction time (min)	Amine value (mg of KOH g of polymer^{-1})
405	0	207.96	435	0	238.178
405	10	198.027	435	10	120.828
405	20	83.114	435	40	60.347
405	60	72.615	435	100	20.686
405	90	57.777	435	210	9.721
405	270	26.133	450	0	252.703
420	0	223.21	450	10	55.724
420	10	132.581	450	40	28.911
420	40	70.427	450	90	16.443
420	90	63.108	450	150	11.072
420	160	50.424	475	0	267.315
420	300	32.866	475	10	49.754
			475	40	36.109
			475	90	16.266
			475	140	11.096

Figure 2 Amount of the condensate produced with time at 435 K: (—) predicted values and (■) experimental values.

Reactor model

The reactor model is based on work of Juha et al.[6] for polyesters. In this model, the mass balance for a component is applied; that for the flow leaving the reactor and the concentrations of ethylenediamine and water will be explained later. The main equations used in this model are as follows:

$$r_i = k_1 C_{COOH} C_{NH_2} - k_2 C_{CONH} C_{H_2O} \tag{2}$$

$$dC_i/dt = r_i + (C_i - w_i/M_i)(dZ/dt)/(1 - Z) \tag{3}$$

$$Z = A[1 - e^{(-Bt)}] \tag{4}$$

$$w_{NH_2} = Ce^{(-Dt)} + E \tag{5}$$

$$w_{H_2O} = 1 - w_{NH_2} \tag{6}$$

$$A = A_1 T + A_2 \tag{7}$$

$$B = B_1 T + B_2 \tag{8}$$

$$C = C_1 T + C_2 \tag{9}$$

$$D = D_1 T + D_2 \tag{10}$$

$$E = E_1 T + E_2 \tag{11}$$

Equation (3) is the mass balance for the reaction. In these equations, k_1 is the second-order rate constant (kg mol^{-1} min^{-1}); k_2 is the reverse rate constant (kg mol^{-1} min^{-1}); C_i is the concentration of the diamine, diacid, or water; t is the reaction time; and r_i is the rate of reaction. Equation (2) is applied before 90% conversion on the basis of a second-order reaction. C_{COOH}, C_{NH_2}, C_{CONH}, and C_{H_2O} are the concentrations of carboxylic acid, ethylenediamine, the amide of amine and carboxylic acid, and water, respectively. w_i is the dimensionless weight fraction of ethylenediamine (i = NH$_2$) or water (i = H$_2$O) in the stream of the condensate, and for the dimer fatty acid, it is assumed to be zero because the boiling point of the dimer fatty acid is relatively high (525 K) and it is assumed no evaporation will take place at this temperatures. These equations are used to take into consideration the evaporation of ethylenediamine during the reaction (boiling point = 392 K), which consequently will affect the rate of reaction. The only components that leave the reactor are water and ethylenediamine. Z in eq. (4) is
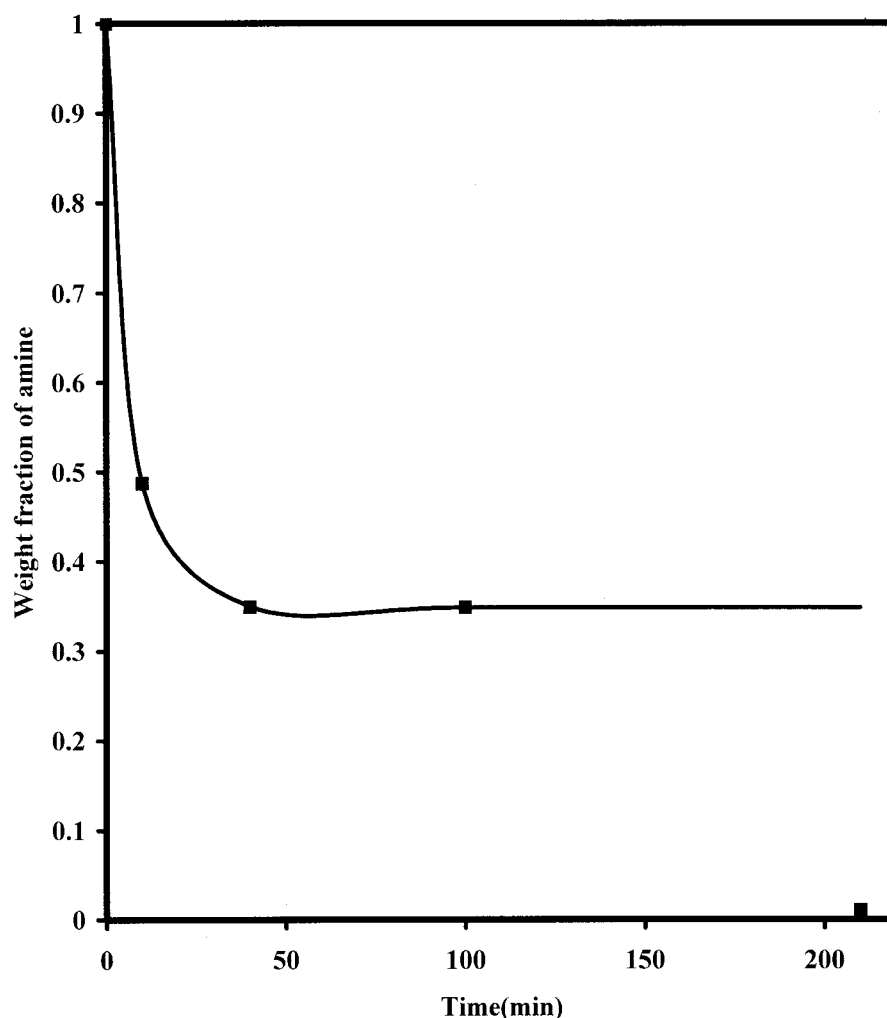
Figure 3 Weight fraction of ethylenediamine with time in a stream of the distillate at 435 K: (—) predicted values and (■) experimental values.

an empirical equation for the total mass of the condensate divided by the total initial mass of the reactants over time.

Equations (5) and (6) are the empirical equations for the weight fractions of ethylenediamine and water in the stream of the condensate with time, respectively. A, B, C, D, and E are constant numbers that can be obtained by a comparison of eqs. (4)–(6) with experimental data with curve-fitting technique. In eqs. (7)–(11), T is the temperature, and these equations are temperature dependences of the aforementioned constants, which can be derived from curve fitting. For the temperature dependences, such as the rate constants and equilibrium constant, the Arrhenius law is applied:

$$k = A_E e^{-(E_{aE}/RT)} \tag{12}$$

where k is the rate constant before 90% conversion (kg mol^{-1} min^{-1}), A_E is the frequency factor (kg mol^{-1}

min^{-1}), E_{aE} is the activation energy (kJ mol^{-1}), and R is the gas constant.

Parameter estimation procedure

The empirical parameters included in the functions for the distillate mass and weight fractions of water and diamine were obtained with nonlinear regression analysis. For the cumulative mass of the distillate, the objective function to be minimized was defined as follows:

$$e_1 = \mathrm{abs}(Z_{j,\mathrm{exp}} - Z_{j,\mathrm{cal}}) \tag{13}$$

where e_1 is the summation of the absolute residual, $Z_{j,\mathrm{exp}}$ is the jth experimental mass of the distillate, and $Z_{j,\mathrm{cal}}$ is the jth calculated mass of the distillate from an empirical equation.

TABLE II
Empirical Parameters for the Distillates [Eqs. (4)–(6)]

T (K)	A	B	C	D	E
405	0.059532	0.074817	0.254123	0.076762	0.745878
420	0.027054	0.029799	0.69071	0.171908	0.309287
435	0.04581	0.058247	0.651501	0.15491	0.348498
450	0.068601	0.078238	0.727907	0.389485	0.272093
475	0.08168	0.175381	0.990005	0.168712	0.009995

$$e_2 = \sum \text{abs}(\text{COOH}_{j,\text{cal}} - \text{COOH}_{j,\text{exp}})^2 \qquad (14)$$

Analogous objective functions were used for the water and amine weight fractions. The objective function was minimized with Excel software (1997) with the solver option, which is based on a reduced gradient method.

The estimation of the rate parameters was performed stagewise. The mass balances were solved numerically during the objective function minimization with the Runge–Kutta method available in

where e_2 is the sum of the residual squares, $\text{COOH}_{j,\text{cal}}$ is the jth concentration of carboxylic acid inside the reactor calculated from the model, and $\text{COOH}_{j,\text{exp}}$ is the jth concentration of carboxylic acid inside the reactor measured experimentally on the basis of acid values. The order of reaction was second-order, as suggested by Vijay et al.[3] for conversions of up to 90% [eq. (2)].
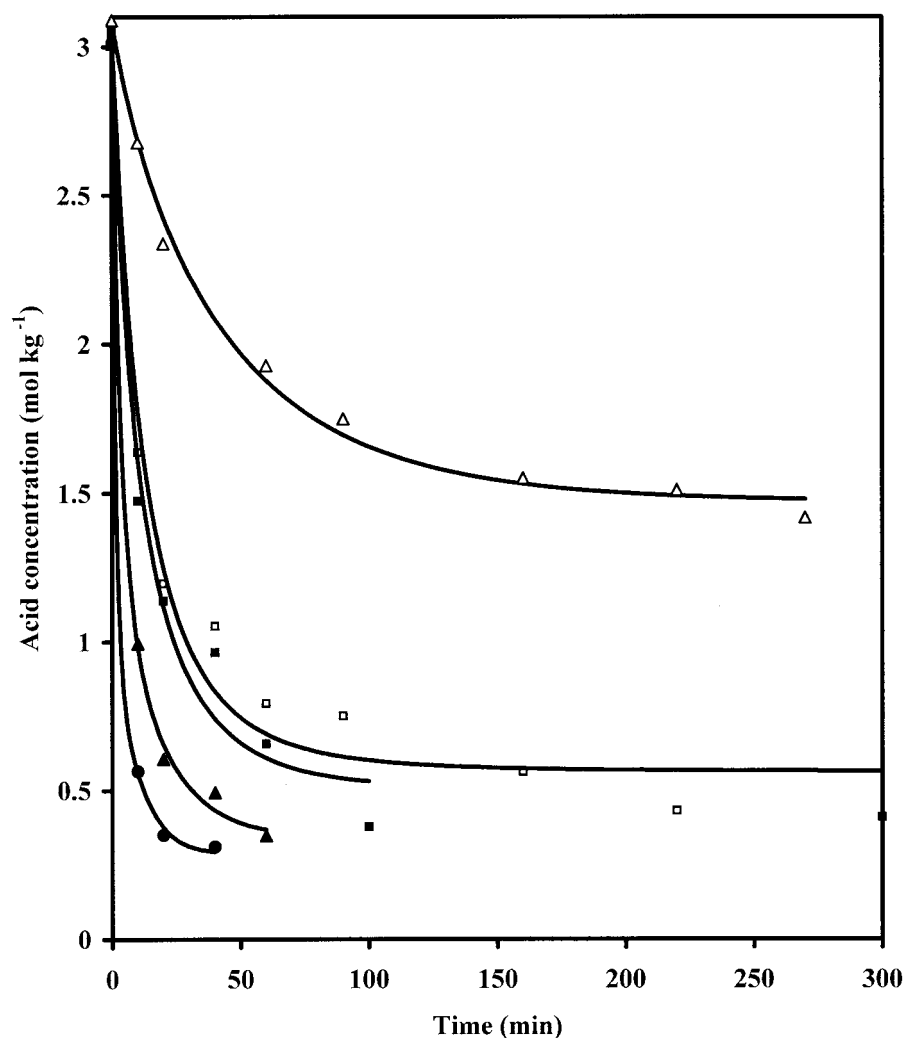

Figure 4 Concentration of carboxylic acid with time: (△) 405, (□) 420, (■) 435, (▲) 450, and (●) 475 K. The continuous lines represent the complete kinetic model before 90% conversion.
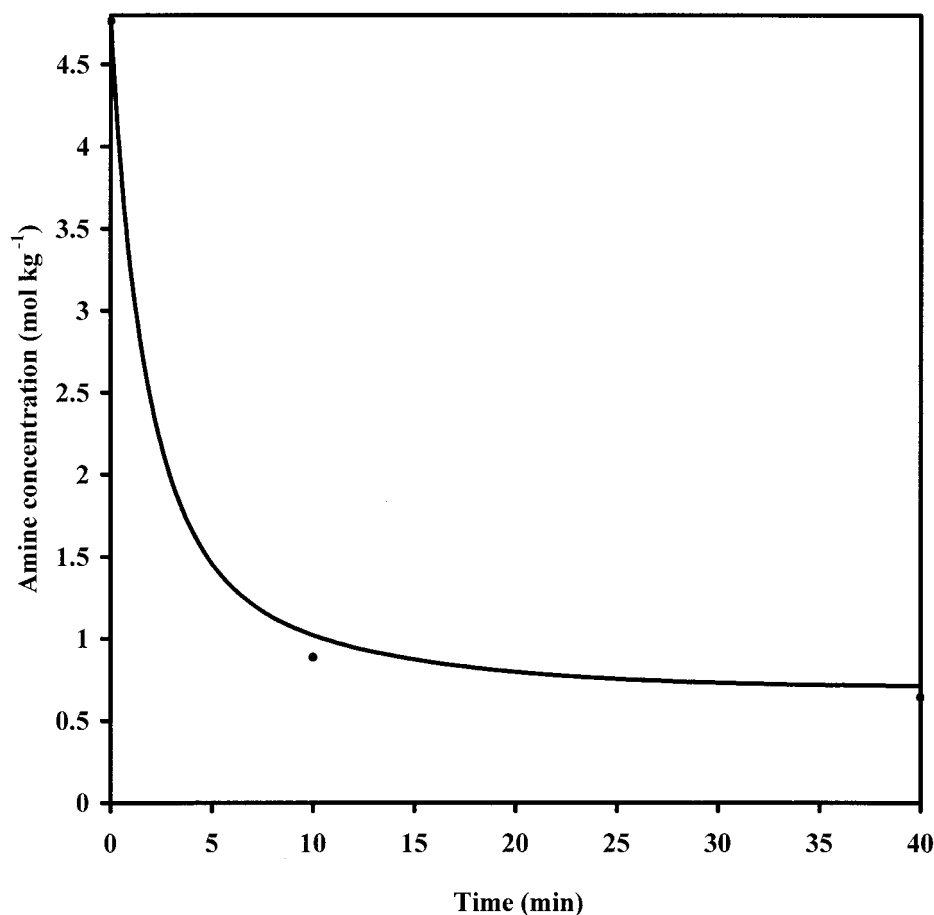
Figure 5 (●) Experimental and (—) predicted concentrations of the amine groups at 475 K.

EXPERIMENTAL

Materials

A dimer fatty acid (Pripol 1013, Uniqema, Guda, The Netherlands), with a purity of 97% (0.1% monomer, 97% dimer, and 3% trimer) and an acid value of 195, was used. The ethylenediamine was laboratory-reagent-grade, with a purity greater than 98%, as determined by titration with standard acid. All other materials were reagent-grade.

Method

The experimental setup, shown in Figure 1, consisted of a 1.5-L stainless steel reactor equipped with a variable stirrer and a nitrogen inlet tube and connected to two condensers. A cooling coil was placed inside the reactor, and the reactor temperature was controlled with an automatic temperature controller. The equipment was connected to a computer for the monitoring of the variations of the temperature and motor speed with time. In a typical operation, 240 g of dimeric fatty acids was charged into the reactor and heated 5 K below the desired temperature. An extra molar amount of ethylenediamine (based on the moles of the dimer fatty acid) was preheated to 391 K and added to the reactor. Extra amine was used to compensate for the amount that evaporated during the preheating process. The amount of ethylenediamine charged at each temperature is given in Table I; it was calculated from initial amine numbers. The stirring speed was set at 75 rpm. A low mixing rate was used to prevent foaming. Moreover, less of the reactant was used to provide enough space in anticipation of foaming. The reaction was carried out at five different temperatures in the range of 405–475 K. Within this temperature range, the materials remained molten. The water generated during the reaction and the evaporated diamine were purged from the reactor with nitrogen at a rate of 20 mL min^{-1}. These materials were later condensed and collected in a prepared container for analysis. The temperature of the cooling water for the condenser was kept at 279 K. The amount of the distillate collected with time was measured, and the sample refractometry index was analyzed with a refractometer (model NAR-1 T; Atago Co., Ltd., Japan). Before that, a calibration curve was established from the measurements of several samples of known
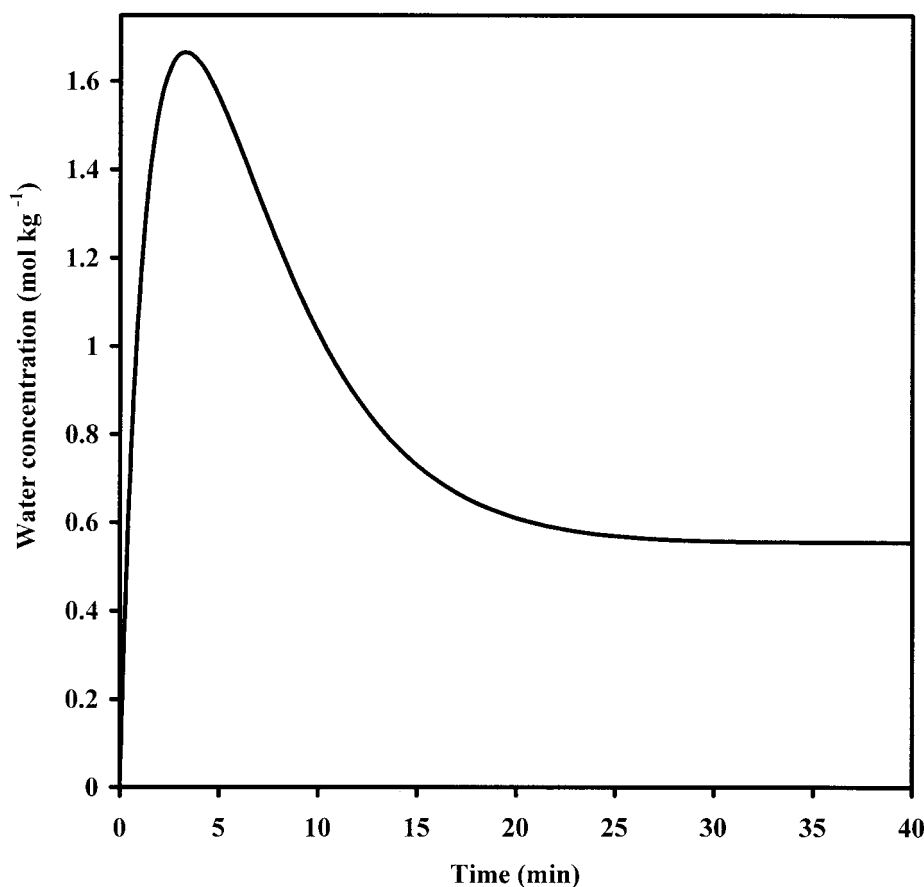
Figure 6 Simulated liquid-phase concentration of water at 475 K.

weight fractions of ethylenediamine in water. The weight fraction of ethylenediamine in the condensate was measured on the basis of the calibration curve.

The samples were taken out of the reactor via a sampling port at several intervals for the analysis of the acid and amine values. The acid value was determined with ASTM D 1980-67 with a neutral solution (1 : 1 v/v) of n-butanol and xylene for the dissolution of the samples. The amine value was determined with ASTM D 2074-62T with the same solvent used for the determination of the acid value.

TABLE III
Kinetic Values of the Rate Constants and Equilibrium Constants

T (K)	k_1 (kg mol^{-1} min^{-1})	k_2 (kg mol^{-1} min^{-1}) before 90% conversion	Absolute deviation percentage	K_E
405	0.0062873555	0.0019296123	4.34	3.258
420	0.017769525	0.0028470260	10.15	6.241
435	0.021226598	0.0037618316	10.99	5.643
450	0.049838420	0.015694744	2.58	3.175
475	0.13026745	0.017818525	1.22	7.311

RESULTS AND DISCUSSION

Modeling of the distillate

At each temperature during the initial part of the reaction, some evaporated ethylenediamine did not condense through the condensers, even though two condensers were used. However, water can be easily condensed, so to measure the total amount of evaporated ethylenediamine, we drowned the samples out of the reactor to analyze them for their amine and acid values. We carried out the sampling processes at several intervals to investigate the changes in the amine and acid values over time. By measuring the evaporation at each time interval, we obtained the difference between the amine and acid values, and we compared it with the difference between the acid and amine value from the previous interval. From the differences of these values with time, the amount of the evaporation during that interval could be obtained. This is because every mole of acid will react with 1 mol of amine, and within this temperature range, the acid does not undergo an evaporation process. Then, theoretically, for each time interval, the difference between the amine and acid value should be constant
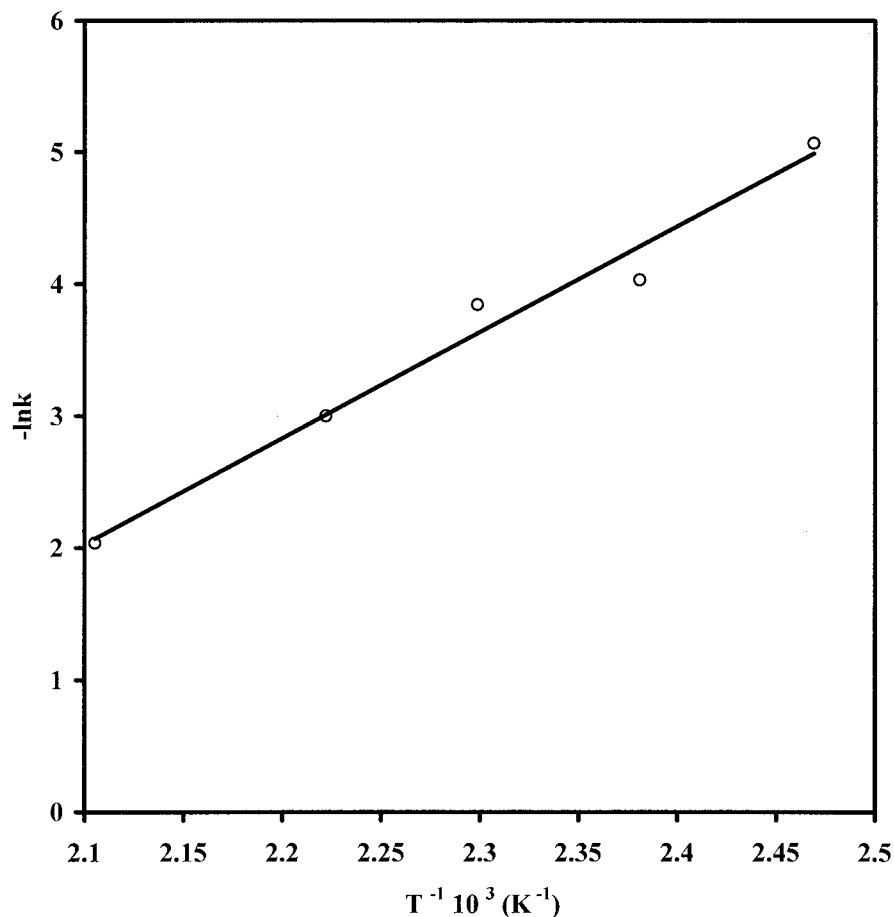
Figure 7 Temperature dependence of the rate parameters before 90% conversion.

unless some of the amine has evaporated. Therefore, if the reduction in the amount of amine is more than the theoretical value, this additional loss can be attributed to evaporation at that time interval. Because some of the ethylenediamine condensed at each time interval, to measure the weight fraction of ethylenediamine out of the total mass of the condensate, we used a refractometry model. From the amount of the amine condensed, the amount of the amine that evaporated but did not condense was calculated. At each time interval, the extra amine had to be added to compensate for the uncondensed amine.

Table I shows the changes in the amine values against time at different temperatures. For all the temperatures, a significant reduction in the initial part of the reaction could be attributed to the evaporation and high rate of the reaction. Figure 4 (shown later) shows the changes in the acid values with the acid concentration. For the acid values, because evaporation did not take place, the decrease in comparison with that of the amine was marginal. The acid and amine values finally were nearly the same during the later stage, and this indicated that the correct amounts of extra amine were added to compensate for the evaporation at the beginning.

Example of the dimensionless mass of the distillate and the weight fraction of the ethylenediamine and the fit of a model for 435 K are shown in Figure 2 and 3, respectively. The general conclusion is that the exponential function applied is suitable for the description of the amount of the distillate and the weight fraction of the diamine in the stream of the condensate. As shown in Figure 2, the amount of the distillate at the beginning increased quickly and then became constant. This was attributed to the fast reaction rate at the beginning due to the high concentrations of the reactants. Figure 3 shows that at the beginning, the weight fraction of the diamine was high, and with increasing reaction time, the weight fraction became

TABLE IV
Arrhenius parameters for the Rate Constants and Equilibrium Constants

Rate constant	A_E	E_{aE} (kJ/mol)
k_1 (before 90% conversion)	2,716,894 (kg mol^{-1} min^{-1})	66.7
K_E	74.4	9.7

less. This was due to the existence of excess free amine at the beginning of reaction in comparison with the later part of the reaction. Juha et al.[6] concluded that for polyesters, analytical data were less accurate for measuring the composition of the distillate. As shown in Figure 3, at the end of the reaction, the weight fraction approached zero, but the exponential equation did not approach zero. The evaporation above 100 min was not effective on the model because at this time interval the flow of the stream of the condensate was almost zero, and so the weight fraction did not affect the model; this can be seen in Figure 2. A list of the empirical parameters is given in Table II. In general, it indicates that the experimental data and model agreed and that the empirical functions used were sufficient to correct the liquid-phase mass balance.

Estimation of the kinetic constants

The fit for the acid concentration with time is presented in Figure 4. The rate of reaction was strongly influenced by the reaction temperature. The results show the reaction obeyed the model well. Figure 5 shows the changes in the amine concentration at 475 K. For the amine concentrations, similar results were obtained at other experimental temperatures. Figure 6 shows the concentration of water, with time, that remained inside the reactor; it reached a constant value after some time, and this was attributed to the evaporation of the produced water. The numerical values of the forward and reverse rate constants and the equilibrium constant before 90% conversion are given in Table III. The results indicate that the reverse rate constant and forward rate constant increased with increasing temperature, as expected, and the absolute percentage of deviation for each of them was below 11%; this shows that the deviation between the model and experiment was low. The aforementioned results show that the equilibrium constant varied randomly with the temperature.

The temperature dependence of the rate parameters for the forward rate constant was tested with Arrhenius plots. The plots are shown in Figure 7, and they show that the rate parameters obeyed the Arrhenius law. Table IV shows the Arrhenius parameters for the rate constants and equilibrium constant. For the equilibrium constant, because the polyamidation reaction was slightly exothermic and the heat of reaction was very low,[8] it can be concluded that the equilibrium constant was independent of the temperature; this can be seen in Table IV, which lists a very low activation energy. We find, by comparing the values obtained with the published values,[2,3,4,5,8–10] that the rate constants and Arrhenius parameters for the forward reaction were nearly comparable; however, for reverse reaction and equilibrium constants, there are no published literature values for comparison.

CONCLUSIONS

A kinetic scheme was proposed for the homogeneous polyamidation of dimer fatty acids and ethylenediamine. Rate laws for these reactions were derived, and the kinetic model was tested by the determination of the kinetic parameters with nonlinear regression analysis. A comparison between the model predictions and actual experimental data showed that the approach was useful and reliable in predicting the progress of polyamidation. The activation energy for the forward rate constant was 66.7 kJ mol^{-1} for conversions up to 90%. The forward and reverse rate constants increased with increasing temperature, and the equilibrium constant was independent of the temperature.

NOMENCLATURE

A	empirical parameter
A_E	frequency factor (kg mol^{-1} min^{-1})
B	empirical parameter
C	empirical parameter
C_i	concentration of i (mol kg^{-1})
$COOH_{j,cal}$	jth concentration of carboxylic acid inside the reactor calculated from the model
$COOH_{j,exp}$	jth concentration of carboxylic acid inside the reactor measured experimentally on the basis of acid values
D	empirical parameter
e_1	summation of the absolute residual
e_2	sum of the residual squares
E	empirical parameter
E_{aE}	activation energy (kJ mol^{-1})
i	component index
j	time index
k	rate constant before 90% conversion (kg mol^{-1} min^{-1})
k_1	second-order rate constant (kg mol^{-1} min^{-1})
k_2	reverse rate constant (kg mol^{-1} min^{-1})
K_E	equilibrium constant
M	molar mass (kg mol^{-1})
M_i	molar mass of i component (kg mol^{-1})
R	gas constant
r_i	rate of reaction
t	time (min)
T	temperature (K)
w_i	dimensionless weight fraction of i
Z	dimensionless mass of the distillate
$Z_{j,exp}$	jth experimental mass of the distillate
$Z_{j,cal}$	jth calculated mass of the distillate from the empirical equation

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