

# Kinetics of reaction of hydrogenated dimer fatty acid C<sub>36</sub> with 2,7 diamino fluorene and determination of thermodynamic constants

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## ABSTRACT

Kinetic studies were carried out on the reaction between 2,7 diamino fluorene and hydrogenated C<sub>36</sub> dimer fatty acid in melt phase. The reaction was performed at 135, 150, 160 and 170°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 48.55 kJ/gmol up to 58, 58, 59 and 60% conversion at 135, 150, 160 and 170°C, then the reaction will become overall third order. The Degree of Polymerization, Number Average Molecular Weight, and Weight Average Molecular Weight have been calculated during different times, relationships between the last properties with time is linear until 58, 58, 59 and 60% conversion at 135, 150, 160 and 170°C, respectively. The kinetic of degradation was carried out by using thermal analysis (TGA). Thermodynamic and equilibrium constants have been defined, where the kinetic of degradation was found to be of overall second order. We have found that the result compound is polyamide by use of infra-red spectroscopy.

**Keywords:** Kinetic, thermodynamic constants, dimer acid.

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## INTRODUCTION

Fatty polyamides are condensation products of di- and polyfunctional amines and di- and poly-basic fatty acids (Ebewele, 1996); the latter are obtained by the polymerization of unsaturated fatty acids or their esters. Fatty polyamides can be broadly classified into two categories: non-reactive and reactive. The non-reactive polyamides have a far lesser number of primary and secondary amine groups to react with epoxy resins compared to the reactive ones. These polyamides also differ in their properties and therefore in their end uses. Non-reactive polyamides are mostly solids and used in the printing ink industry, thermosetting and adhesives (Brydson, 1999). The reactive polyamides are mostly liquid and used in the surface coatings, and adhesives industry (Fan et al., 1998; Chen et al., 2002). Dimer acid-based polyamides were prepared due to their singular molecular structure based on their, the dimer acid show relatively good performance (Hablott et al., 2010; Brandrup et al., 1999). Most of the literatures on fatty polyamide preparation are patented (Brydson, 1999; Fan

et al., 1998; Deng et al., 1999). Non-reactive polyamides were prepared by reacting a mixture comprising polymeric fatty acids, and diamines such as ethylenediamine, hexamethylenediamine, and an aliphatic monobasic acid or amine, to obtain a product of the desired extent of reaction, degree of polymerization, number average molecular weight, viscosity, and softening point. Most of these polyamides have properties comparable to the commercially available polyamides used in flexographic inks, adhesives and overprint varnishes (Vedanayagam and Kale, 1992). Renewable biocomposites of dimer fatty acid-based polyamides with cellulose fibers were prepared and their thermal, physical, mechanical properties and yield behaviour, and high strain rate behaviour, were studied (Averous et al., 2010; Matadi et al., 2011; Vaudemond et al., 2010). The influence of monofunctional reactants on the physical properties of dimer acid-based polyamides was studied where Dimer acid-based polyamides were synthesized by condensation polymerization in the

absence and presence of monofunctional reactants. Acetic acid, oleic acid and propylamine were used as monofunctional reactants (Cavus et al., 2006). Much of the literature has been reported on the kinetics of this reaction such as nylon 6 and nylon 6,6 (Guidici, 1999) and reaction of dimeric fatty acids  $C_{36}$  with Ethylenediamine at 124, 130, 145, 160, 174 and 190°C (Kale et al., 1988), as well as the reaction between ethylenediamine and dimer fatty acids in benzyl alcohol solution at 160 to 190°C (Vedanayagam et al., 1992). A generally applicable stoichiometric and kinetic model was developed for the polymerization of dimer fatty acid with Ethylenediamine, comparison of the model prediction with the experimental data showed that the approach is useful in the predicting the polymerization kinetic (Heidarian et al., 2003). A generally applicable stoichiometric and kinetic model was developed for the polymerization of dimer fatty acid with Ethylenediamine in melt phase in the presence of phosphoric acid as catalyst at 132 to 202°C (Heidarian et al., 2004), the reaction kinetics between ethylenediamine and dimeric fatty acids was studied in melt phase in the range of 162 to 202°C above 90% conversion (Heidarian et al., 2005). Thermal analysis refers to a variety techniques in which a property of a sample is continuously measured as the sample is programmed through a predetermined temperature profile. Endothermic and exothermic reactions or phase changes in the sample undergo to changes in temperature between the sample and the furnace to more than one degree (Chermisnoff, 1996). There are many methods of thermal analysis, but the present discussion will be limited only in the techniques that are used in determining the properties of polymers, which are: thermal gravimetric analysis (TGA, in TGA makes a continuous weighing of a small sample in a controlled atmosphere (nitrogen) as the temperature is increased at a programed linear rate. Thermogram shown in Figure 7 illustrates loss in weight. In recent years, from applications of TGA, study the kinetics of degradation for compounds. But, no work has been reported on the kinetics of this reaction in melt phase for preparing dimer acid-based polyamides with 2,7 Diamino Fluorene, and the kinetics of the degradation by use. TGA and determination thermodynamic constants, in our work we will study kinetics of this reaction in melt phase for preparing dimer acid-based polyamides with 2,7 Diamino Fluorene, and we will apply technique of TGA, for kinetics of the degradation and determine the thermodynamic constants.

## EXPERIMENTAL

### Materials

Hydrogenated dimer fatty acid  $C_{36}$  (bottle 2 L from Sigma-Aldrich) 97% purity and density of 0.95 g/ml, while 2,7

diamino fluorene is solid (powder), its color is dark brown, it was laboratory reagent grade having purity of above 98%.

### Method

A 1-L round bottom Flask, equipped with stirrer, nitrogen inlet tube, thermo well, Dean-Stark apparatus and addition funnel, was charged with known weight of dimeric fatty acid and heated in an isomantle. An equivalent molar quantity of 2,7 diamino fluorene was added within 2 min, and the heating was regulated to get the desired temperature within 15 min. The polyamidation reaction was carried out at five different temperatures in the range of 135 to 170°C. In this temperature range, the reaction mass remained in molten state. The water generated during the reaction was swept out of the system by nitrogen bubbled through the reacting melt 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. The acid values were determined using a neutral solution (50/50, v:v) of methanol and tetrahydroforan for dissolving the samples and then the degree of polymerization, number average molecular weight and weight average molecular weight have been calculated during different times, when the reaction have finished the kinetic of degradation for result polyamide were carried out by use of thermal analysis (TGA), thermodynamic constants for degradation were defined by use thermal analysis (TGA), infra-red (IR) spectroscopy was used for determination of resulting compound structure.

### FT-IR measurements

Polyamide was thoroughly ground with KBr (IR, grade, Merck-Germany) (at a ratio of 1:200) and pressed into a pallet and then the spectrum was recorded.

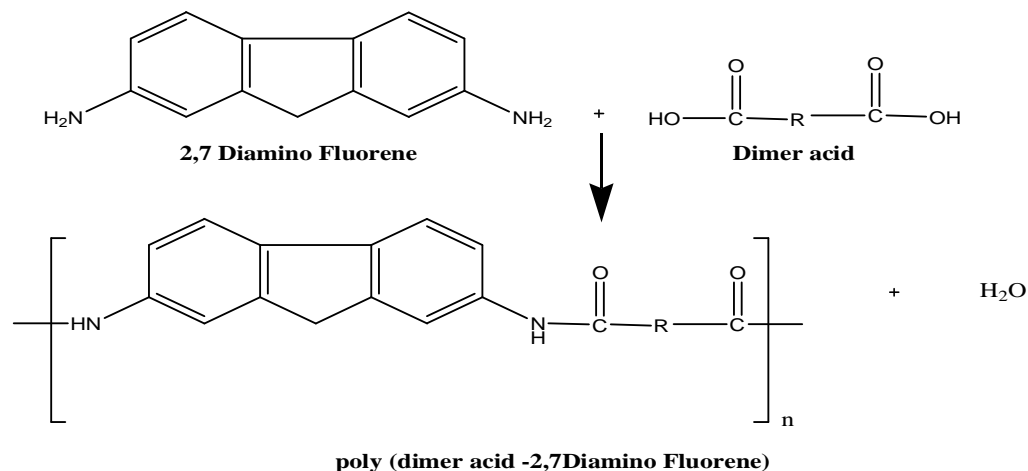
### Differential scanning calorimetry (TGA)

TGA measurements were carried out at a heating rate of 10°C/min under nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Preparation of polyhydrogenated dimer fatty acid $C_{36}$ with 2,7 diamino fluorene

Polyamide was prepared from Hydrogenated dimer fatty acid  $C_{36}$  and 2,7 diamino fluorene as in following reaction:



The polyamidation reaction in melt phase was carried out at 135, 150, 160 and 170°C and was followed by determining the acid values of the product at each temperature. The reaction could be followed by the fall in acid value (Kale et al., 1988; Vedanayagam et al., 1992; Heidarian et al., 2003, 2004, 2005). The variation in acid values with reaction time is tabulated in Table 1. The integral method of analysis was used for studying the kinetics of the reaction. Based on the data available in the literature (Kale et al., 1988; Vedanayagam et al., 1992; Heidarian et al., 2003, 2004, 2005) on kinetics of other polyamidation reaction 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. Since the equivalent amounts of the acid and amine were taken initially and the reaction is homogeneous, the reaction rate for a second order reaction is as follows:

When:  $A + B \rightarrow \text{Product}$  then  $\frac{dx}{dt} = k_2(a-x)(b-x)$

Or:  $2A \rightarrow \text{Product}$  then  $\frac{dx}{dt} = k_2(a-x)^2$  (1)

Thus, the following equation is used for the second order kinetics:

$$\frac{1}{C_A} - \frac{1}{C_{A_0}} = kt$$

Where  $C_{A_0}$  and  $C_A$  are the carboxyl end group contents present initially and at time  $t$  (min), respectively, expressed as  $\text{m.mol kg}^{-1}$ ,  $k$  is the second order rate constant expressed as  $(\text{m.mol kg}^{-1})^{1-n}(\text{time})^{-1}$ , and  $t$  is the

**Table 1.** Reaction rate constants at various temperatures.

T (°C)	T (K)	1/T (K <sup>-1</sup> )	(con) <sup>1-n</sup> (time) <sup>-1</sup> k
135	408	0.002451	$8.83 \times 10^{-5}$
150	423	0.002364	$1.19 \times 10^{-4}$
160	433	0.002309	$1.71 \times 10^{-4}$
170	443	0.002257	$2.80 \times 10^{-4}$

reaction time (min). If  $(AV)_0$  and  $AV$  are the acid values (mg KOH/g polymer) at time  $t = 0$ , that is, the time at which both the reactants are brought into contact, and at time  $t$  (min), respectively, then  $C_{A_0}$  and  $C_A$  can be expressed as:

$$C_{A_0} = \frac{10^3(AV)_0}{56.1} \quad \text{and} \quad C_A = \frac{10^3(AV)}{56.1} \quad (2)$$

Hence, Equation 1 can be written as:

$$\frac{1}{A_V} - \frac{1}{A_{V_0}} = \frac{kt}{0.0561}$$

Using Equation 2 for a second order reaction, a plot of  $1/AV$  vs. time was drawn and found to fit the equation quite well up to about 58, 58, 59 and 60% conversion at 135, 150, 160 and 170°C, respectively, the temperatures were studied as shown in Figures 1 and 2.

In Figures 1 and 2, it is shown that the polyamidation reaction follows second-order kinetic up to the last conversion. It has also been reported in the literature (Kale et al., 1988; Vedanayagam et al., 1992; Heidarian et al., 2003, 2004, 2005) that the results of the polyamidation reaction were carried out under conditions in which the end group concentrations are relatively low (e.g., conversions above last conversion) indicate that a carboxyl-catalyzed third-order reaction assumes

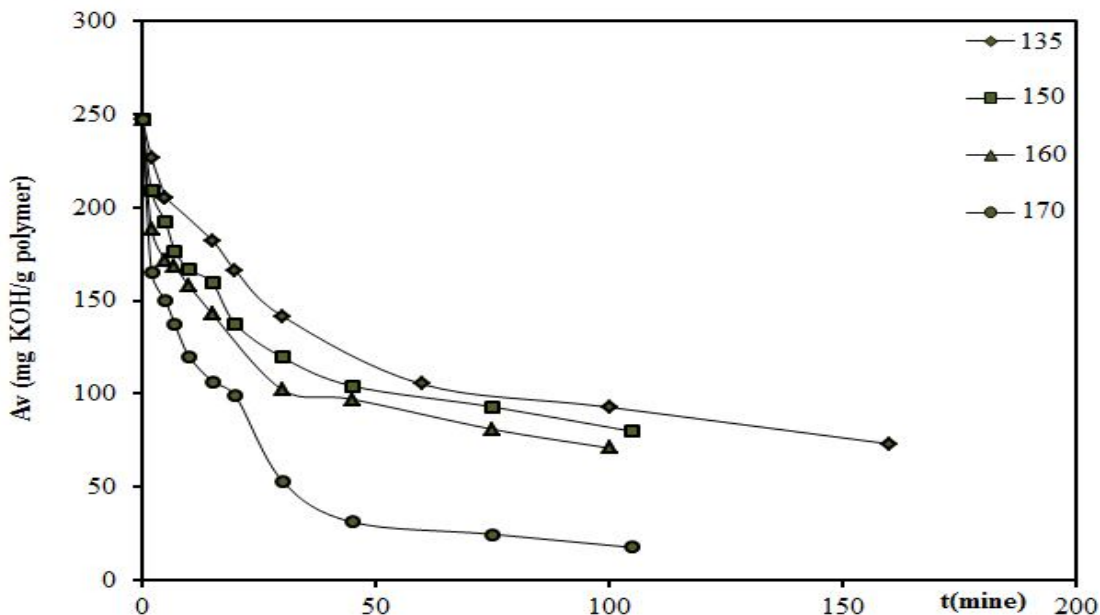


Figure 1. Changes in acid value with time at studied temperatures.

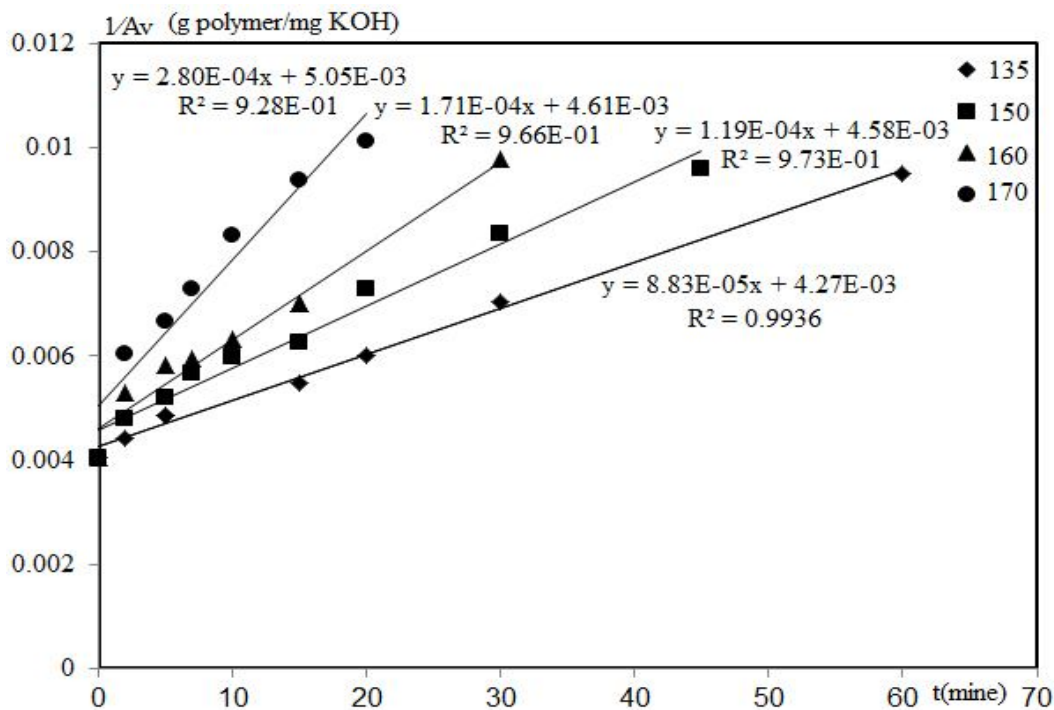


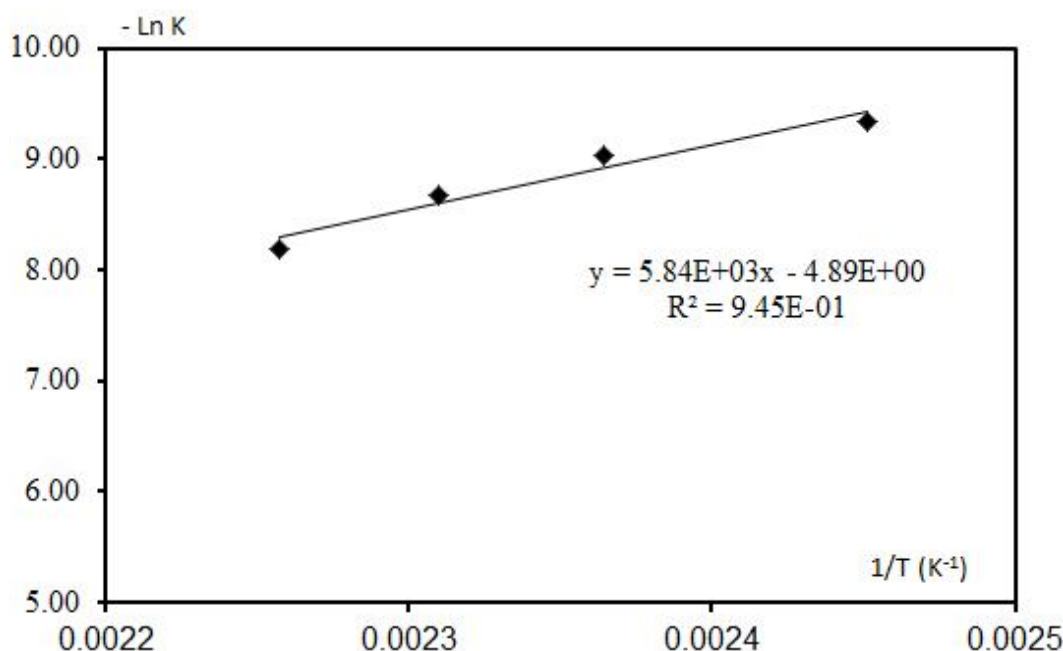
Figure 2. Changes in (1/Av) with time at studied temperatures.

increasing importance and becomes predominant. Hence, it was assumed that the reaction would follow an overall third-order kinetics above last conversion, which is second order with respect to the acid group concentration and first order with respect to the amino group

concentrations since the carboxyl and amino group concentrations are equal. The second order reaction rate constants calculated by the least square analysis of the data of Figure 2 are given in Table 2. These rate constants were found to fit the Arrhenius well as shown in

**Table 2.** Variations of conversion degree, the number average of molecular weight, and polymerization degree with reaction time at 135°C.

t (min)	M <sub>n</sub> (g/mole)	M <sub>w</sub> (g/mole)	X <sub>n</sub>	P%
0	730.25	730.25	1.00	0.000
2	798.25	866.26	1.09	0.085
5	881.57	1032.90	1.21	0.172
15	992.39	1254.53	1.36	0.264
20	1088.53	1446.81	1.49	0.329
30	1276.09	1821.92	1.75	0.428
60	1720.14	2710.04	2.36	0.575
100	1949.50	3168.74	2.67	0.625
160	2472.71	4215.17	3.39	0.705



**Figure 3.** Change in -Log K with temperatures reverse.

Figure 3; the Arrhenius equation is:

$$k = A \exp^{-E_a/RT_s}$$

where, k = reaction rate constant [(m.mol Kg<sup>-1</sup>)<sup>1-n</sup>(time)<sup>-1</sup>], T<sub>s</sub> = absolute temperature, E<sub>a</sub> = activation energy (kJ/gmol), A: pre-exponential factor [(m.mol kg<sup>-1</sup>)<sup>1-n</sup>(time)<sup>-1</sup>] where n is: order of reaction, R = gas constant.

$$\text{Ln}k = \left( -\frac{E_a}{R} \right) \left( \frac{1}{T_s} \right) + \text{Ln}A \quad (4)$$

Rate constants were shown in Table 1. The activation

energy for the second order reaction was calculated from the least square analysis of the data of Figure 3 and was found to be 48.55 kJ/gmol.

#### Molecular weights for prepared polyamides

The molecular weight is considered one of the most important properties of polymers that depend on most mechanical and physical properties of polymer besides to other technological usages. Strength and elasticity of polymers are due to interfusion and hitching of the polymeric long gamuts with each other. The molecular weights of elasticity polymers should be higher than adhesives which have less weight relatively. So, dominance of molecular weights during the production is very important.

**Table 3.** Variations of conversion degree, the number average of molecular weight, and polymerization degree with reaction time at 150°C.

t (min)	M <sub>n</sub> (g/mole)	M <sub>w</sub> (g/mole)	X <sub>n</sub>	P%
0	730.25	730.25	1.00	0.000
2	866.22	1002.18	1.19	0.157
5	941.78	1153.31	1.29	0.225
7	1023.29	1316.33	1.40	0.286
10	1084.39	1438.53	1.48	0.327
15	1133.45	1536.65	1.55	0.356
20	1316.39	1902.53	1.80	0.445
30	1511.27	2292.29	2.07	0.517
45	1735.78	2741.31	2.38	0.579
75	1945.09	3159.92	2.66	0.625
105	2266.29	3802.33	3.10	0.678

**Determination of conversion degree**

The conversion degree (*P*) (Braun, 2001) is determined according to the following equation:

$$P = \frac{A_{v_0} - A_v}{A_{v_0}} \times 100 \tag{5}$$

Where:

A<sub>v0</sub>: the acid number in the time t<sub>0</sub> (before reaction)  
 A<sub>v</sub>: the acid number in the time t

**Determination of number and weight averages of molecular weight**

The number average of molecular weight (*M<sub>n</sub>*) (Braun, 2001) is determined according to the following equation:

$$M_n = X_n M_0 = \frac{M_0}{(1 - p)} \tag{6}$$

$$X_n = \frac{M_0}{(1 - p)} \tag{7}$$

Where:

P: conversion degree  
 M<sub>0</sub>: the molecular weight for monomer  
 X<sub>n</sub>: The polymerization degree

Where the weight average of molecular weight (*M<sub>w</sub>*) (Braun, 2001) is determined according to the following equation:

$$M_w = M_0 X_w \tag{8}$$

$$X_w = \frac{1 + P}{1 - P} \tag{9}$$

Where:

P: conversion degree  
 M<sub>0</sub>: the molecular weight for monomer  
 X<sub>w</sub>: the weight-average degree of polymerization

**Determination of polymerization degree**

The polymerization degree (*X<sub>n</sub>*) (Braun, 2001) is determined and calculated according to the following equation:

$$X_n = \frac{M_n}{M_0} \tag{10}$$

Tables 2, 3, 4 and 5 show the values of conversion degree, the number average of molecular, weight and polymerization degree through the time of studied temperatures.

Table 5 shows that the polymerization degree has been become 14.13, the number average of molecular weight is 10320.87 and the weight average of molecular degree is 19911.48 at 145°C whereas polymerization degree ranged between 3.06 and 14.13.

The relationship between the number average of molecular weight, the weight average of molecular weight, and polymerization degree with time is shown in Figures 4, 5 and 6 where it was found linear until 58, 58, 59 and 60% conversion at 135, 150, 160 and 170°C, respectively.

We notice from the previous forms that all of number average of molecular weight, the weight average of molecular weight and the degree of polymerization increase gradually with time; it is due to the growth of

**Table 4.** Variations of conversion degree, the number average of molecular weight, and polymerization degree with reaction time at 160°C.

t (min)	M <sub>n</sub> (g/mole)	M <sub>w</sub> (g/mole)	X <sub>n</sub>	P%
0	730.25	730.25	1.00	0.000
2	960.41	1190.58	1.32	0.240
5	1052.96	1375.66	1.44	0.306
7	1075.09	1419.93	1.47	0.321
10	1144.38	1558.51	1.57	0.362
15	1266.38	1802.50	1.73	0.423
30	1768.79	2807.33	2.42	0.587
45	1862.92	2995.58	2.55	0.608
75	2233.50	3736.75	3.06	0.673
100	2551.83	4373.42	3.49	0.714

**Table 5.** Variations of conversion degree, the number average of molecular weight, and polymerization degree with reaction time at 170°C.

t (min)	M <sub>n</sub> (g/mole)	M <sub>w</sub> (g/mole)	X <sub>n</sub>	P%
0	730.25	730.25	1.00	0.000
2	1094.01	1457.77	1.50	0.333
5	1206.25	1682.25	1.65	0.395
7	1317.75	1905.26	1.80	0.446
10	1504.43	2278.62	2.06	0.515
15	1695.06	2659.87	2.32	0.569
20	1831.49	2932.74	2.51	0.601
30	3397.29	6064.32	4.65	0.785
45	5805.49	10880.73	7.95	0.874
75	7340.72	13951.18	10.05	0.901
105	10320.87	19911.48	14.13	0.929

polymer chains.

### Thermal study and kinetic and thermodynamic parameters

Since we cannot obtain thermodynamic parameters ( $\Delta H$ ,  $\Delta G$ ,  $\Delta S$ ) through reactions at different temperatures, we resort to study the thermal degradation using the technique of thermogravimetric analysis (TGA). TGA curves recorded for the successive steps of the processes of degradation of the polyamide, so we must determine the parameters for each step in the reaction: ( $T_b$ ): is the elementary temperature at which degradation begins; ( $T_f$ ): is the finality temperature at which degradation finished;

( $T_{max}$ ): is the maximum temperature of the loss in the mass, it determined of the tangent for the TGA curve.

We weigh very small amount of polymer (8.2174 mg) in a small pot of aluminum and placed in oven of the device, the device programmed thermally so that the heating rate of 10°C/min and it was recorded continuous change of the mass for the temperature under a controlled atmosphere of nitrogen. TGA curve shows the loss weight as a result of the degradation of the sample. Figure 7 illustrates TGA curve of the studied polymer.

Thermal analysis uses in study the kinetic of degradation by using the equation of Coats-Redfern (Maitra, et al., 2008; Shehap, 2008). The kinetic and thermodynamic parameters of thermal degradation process have been calculated using Coats-Redfern relation is as follows:

$$\text{Log} \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \text{Log} \frac{AR}{qE_a} \left[ 1 - \frac{2RT}{E_a} \right] - \frac{E_a}{2.303RT} \quad \text{for } n \neq 1 \quad (11)$$

$$\text{Log} \left[ \frac{-\text{Log}(1-\alpha)}{T^2} \right] = \text{Log} \frac{AR}{qE_a} \left[ 1 - \frac{2RT}{E_a} \right] - \frac{E_a}{2.303RT} \quad \text{for } n=1 \quad (12)$$

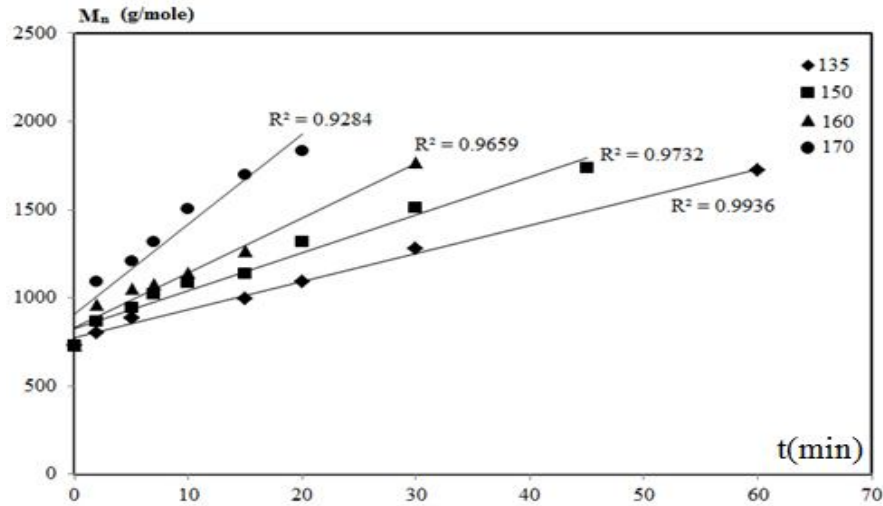


Figure 4. Change in the number average of molecular weight with time at studied temperatures.

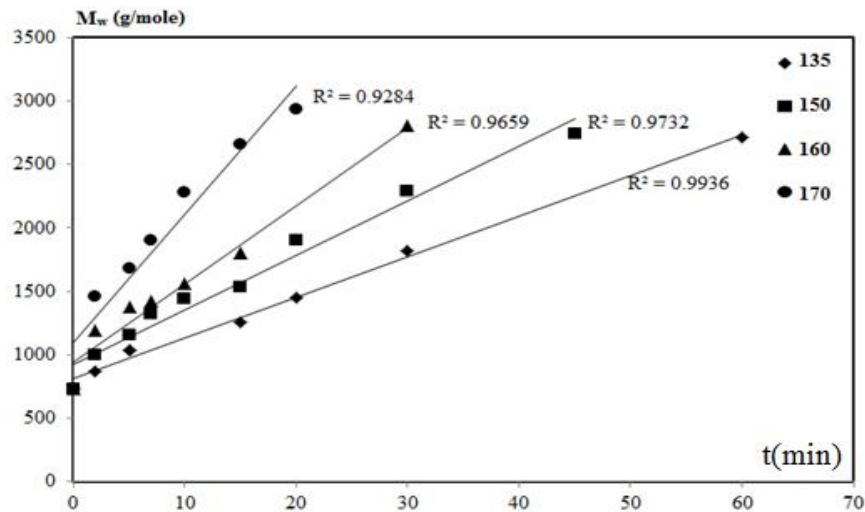


Figure 5. Change in the weight average of molecular weight with time at studied temperatures.

Where  $\alpha$  represents the fraction of sample decomposed at time  $t$ ,  $n$  is the order of the reaction,  $T$  is the temperature (K),  $A$  is the pre-exponential,  $E_a$  is the activation energy (Maitra, et al., 2008; Shehap, 2008).  $R$  is the gas constant,  $q$  is the heating rate.

The activation energy was calculated from the slope of the result line from drawing  $\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$  vs  $1/T$ ,  $A$  is the Arrhenius factor determined from the secant to the

axis Y, this method is an integral method that assumes various orders of reaction and compares the linearity in each case to select the correct order (Tonbul and Yurdakoj, 2001).

Tables 6, 7 and 8, and Figure 8, 9 and 10, illustrate

values  $\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$  vs.  $1/T$  for  $n = 2$ :

From the slope the result line from drawing



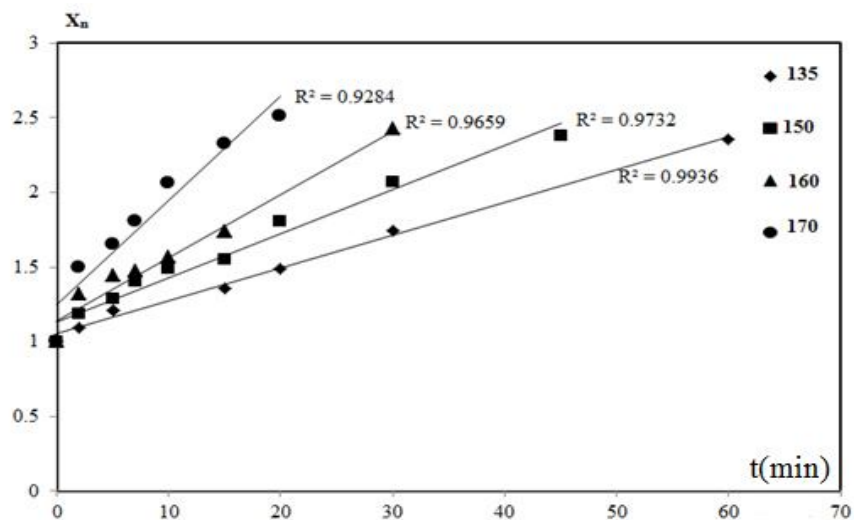


Figure 6. Change in polymerization degree with time at studied temperatures.

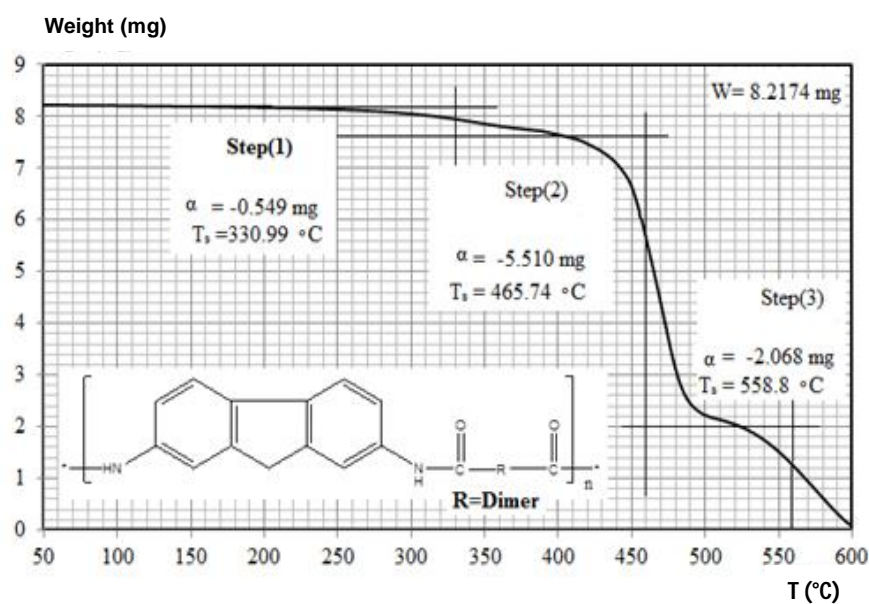


Figure 7. TGA curve of the studied polymer.

Table 6. Values  $\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$  vs.  $1/T$  for  $n = 2$ , Step (1,  $\alpha = 6.676\%$ ).

T (K)	1/T (K <sup>-1</sup> )	$\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$	Slope
553	0.001808	-6.63093	543.943
593	0.001686	-6.69159	
633	0.00158	-6.74828	
673	0.001486	-6.80151	
713	0.001403	-6.85166	

Table 7. Values  $\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$  vs.  $1/T$  for  $n = 2$ , Step (2,  $\alpha = 67.054\%$ ).

T (K)	1/T (K <sup>-1</sup> )	$\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$	Slope
733	0.001364	-5.42159	653.740
743	0.001346	-5.43336	
753	0.001328	-5.44497	
763	0.001311	-5.45643	
773	0.001294	-5.46774	

**Table 8.** Values  $\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$  vs.  $1/T$  for  $n = 2$ , Step (3,  $\alpha = 25.169\%$ ).

T (K)	1/T (K <sup>-1</sup> )	$\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$	Slope
793	0.001261	-6.27176	722.422
813	0.00123	-6.2934	
833	0.0012	-6.31451	
853	0.001172	-6.33511	
873	0.001145	-6.35524	

**Tables 9.** Values of Arrhenius equation for degradation.

Rate constants	Step 1	Step 2	Step 3
T <sub>s</sub> (K)	603.99	738.74	831.8
E <sub>a</sub> (kJ/mol)	10.415	12.517	13.832
A (mol <sup>-1</sup> . min <sup>-1</sup> )	0.030	2.691	81.576
k (mol <sup>-1</sup> . min <sup>-1</sup> )	0.004	0.351	11.038

**Table 10.** Values activation energy and thermodynamic and equilibrium constants.

Thermodynamic constants	Step 1	Step 2	Step 3	Step (1+2+3)
T <sub>s</sub> (K)	603.99	738.74	831.8	-
α (%)	6.676	67.054	25.169	-
E <sub>a</sub> (kJ/mol)	10.415	12.517	13.832	36.764
ΔS (kJ/mol K)	-0.280	-0.244	-0.217	-0.741
ΔH (kJ/mol)	5.393	6.375	6.917	18.685
ΔG (kJ/mol)	174.536	186.823	187.320	548.679
K <sub>eq</sub>	8.037 × 10 <sup>-16</sup>	6.161 × 10 <sup>-14</sup>	1.724 × 10 <sup>-12</sup>	4.403 × 10 <sup>-14</sup>

$\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$  vs  $1/T$ , we obtained the activation energy from the equation  $E_a = 2.303mR$ , pre-exponential factor determined from the secant, we notice from the last forms that  $R^2 = 0.999$  for the degradation of the first and third stage and  $R^2 = 0.9998$  for degradation of the second stage in both cases; Table 9 illustrates values of Arrhenius equation for degradation.

The entropy is calculated from the equation:

$$\Delta S^* = R \ln \frac{Zh}{KT_s} \tag{13}$$

Where  $k$  and  $h$  are the Boltzmann and Planck constants respectively,  $T_s$  is the maximum temperature of the loss in the mass of the curve of TGA.

The Gibbs free energy ( $\Delta G$ ) and enthalpy ( $\Delta H$ ) are calculated from the equations:

$$\Delta H^* = E_a - RT_s \tag{14}$$

$$\Delta G^* = \Delta H^* - T_s \Delta S^* \tag{15}$$

The relationship between Gibbs free energy and equilibrium constant are given with:

$$\Delta G^\circ = -RT \ln K_{eq} \tag{16}$$

R: gas constant, T: temperature (K), K<sub>eq</sub>: equilibrium constant.

The total equilibrium constant for degradation composed of three steps is given with:

$$K_{eq} = (K_{eq1} K_{eq2})^{\frac{1}{2}} \tag{17}$$

The activation energy and thermodynamic and equilibrium constants have been calculated according to the last equations. Table 10 illustrates the values.

Since the reaction is endothermic, and this is illustrated values ( $\Delta H$  positive) which we have obtained in Table 10, as the degradation occur by heating (endothermic), it gives a more regular particles ( $\Delta S$  negative), we have noticed its negative values in the table (the resulting compound is solid). If change of entropy was positive the sample would not be solid, and thus the reaction occur coercive (the degradation forced to occur by heating) ( $\Delta G$  positive), we have got very small equilibrium constant due to the reaction is endothermic (the reaction is not perfect), the reaction is speed because it occur at high temperature.

### Infra-red spectrum

The infra-red spectrum of 2,7 diamino fluorene and dimer acid-based polyamide was scanned using a device (FTIR) and mixed with KBr, and films were made and

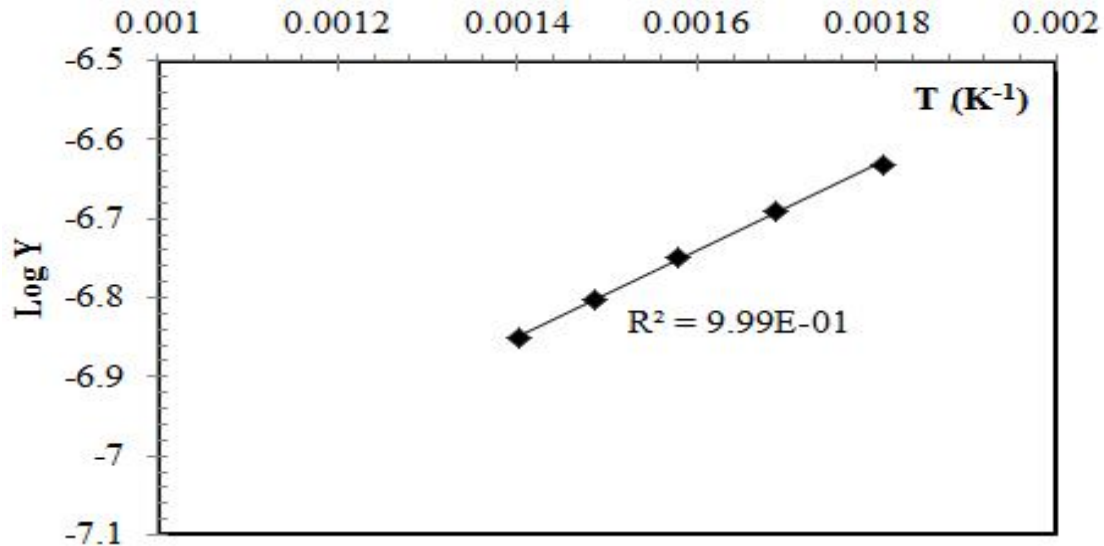


Figure 8. Change in Log Y =  $\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$  with temperatures reverse.

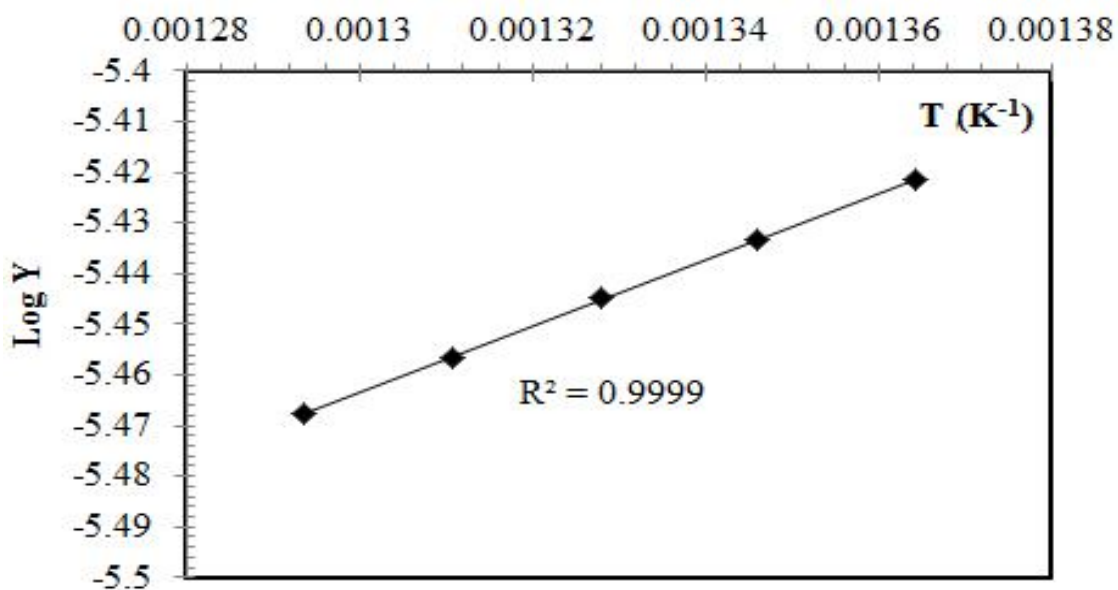


Figure 9. Change in Log Y =  $\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$  with temperatures reverse.

scanned; Figure 11 illustrates the infra-red spectrum for polyamide.

Figure 11 illustrates stretching band at  $1655.1 \text{ cm}^{-1}$  due to group CO, where the bond N-H have stretching band at  $1541.7 \text{ cm}^{-1}$ , the present bands at  $618.8 \text{ cm}^{-1}$  due to methylene groups in dimer acid, while the absorption band of N-H appears at a wavelength  $3418.8 \text{ cm}^{-1}$  (Cho et al., 1997, 1999; Zhang et al., 2002; Bajpai and Khare, 2004). It is known that N-H and O-H absorption bands

are seen at the same region,  $3100 \text{ to } 3600 \text{ cm}^{-1}$ , as sharp and broad bands, respectively. The sharp bands are seen in the spectra of polyamides are assigned to N-H groups that are hydrogen bonded to C=O groups. The intensity of non-hydrogen-bonded N-H stretching seen at  $3418.8 \text{ cm}^{-1}$  as a broad shoulder in the spectrum of polyamide, the sharp hydrogen-bonded N-H stretching band disappeared and instead, a broad band at  $3418.8 \text{ cm}^{-1}$  attributed to non-hydrogen-bonded N-H stretching

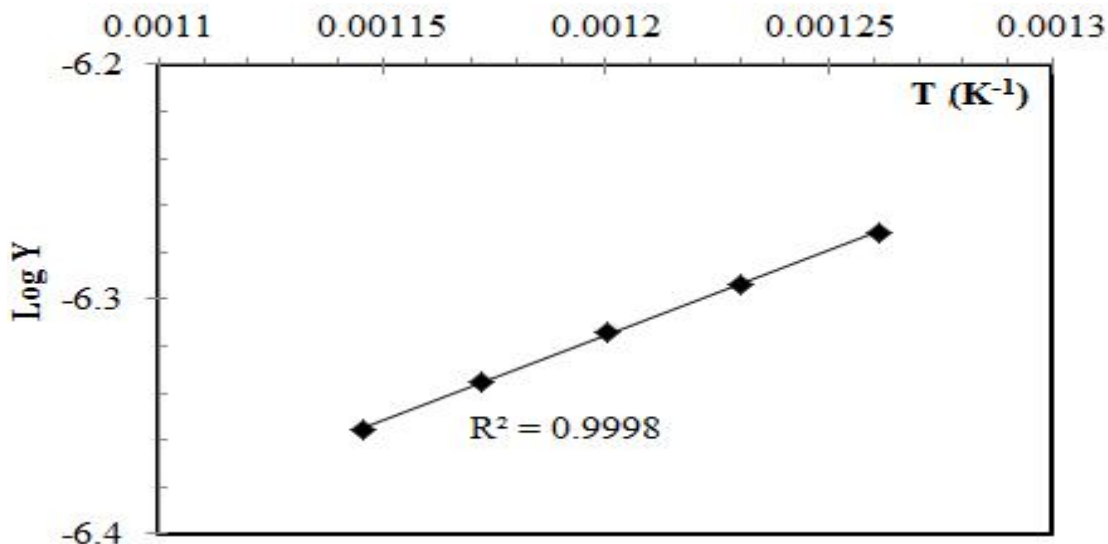


Figure 10. Change in  $\text{Log } Y = \log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right]$  with temperatures reverse.

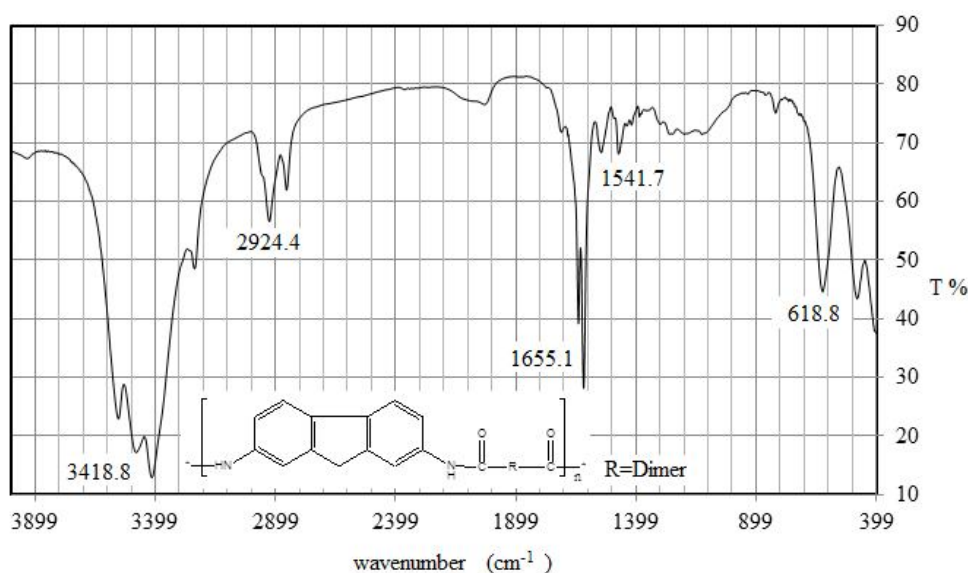


Figure 11. Infra-red spectrum for resulted polyamide.

appeared.

**CONCLUSIONS**

1. The melt phase polyamidation reaction follows an overall second-order kinetics up to 58, 58, 59 and 60% conversion at 135, 150, 160 and 170°C with activation energy of 48.55 kJ/gmol.
2. The relationship between the number average of molecular weight, the weight average of molecular

- weight, and polymerization degree is shown with time where it was found linear 58, 58, 59 and 60% conversion at 135, 150, 160 and 170°C respectively in all studied temperatures.
3. The kinetic of degradation was found to be of overall second order. Where the high values of the energy of activation reveals the high stability as well as the negative values of  $\Delta S$  for the degradation process indicates more ordered activated polyamide than the reactants or the reaction is slow. Moreover, the positive sign of  $\Delta G$  reveals that the decomposition steps are non-

spontaneous process.

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## REFERENCES

- Averous L, Hablot E, Matadi R, Ahzi S, 2010. Renewable biocomposites of dimer fatty acid-based polyamides with cellulose fibres: thermal, physical and mechanical properties. *Compos Sci Technol*, 70:504-509.
- Bajpai A, Khare K, 2004. Direct polycondensation of castor oil based dimer acid and aromatic diamines using triphenyl-phosphite. *J Macromol Sci Pur Chem*, A41(3):275-293.
- Brandrup J, Immergut EH, Grulke EA, Abe A, Bloch DR, 1999. *Polymer Handbook*. Wiley-Interscience: 4<sup>th</sup> Ed. New York.
- Braun D, Cherdrion H, Ritter H, 2001. *Polymer synthesis: theory and practice*. Springer-verlag berlin Heidelberg, New York, p. 221.
- Brydson JA, 1999. *Plastics Materials*. University of North, London, p 478- 480.
- Cavus S, Gurkaynak MA, 2006. Influence of monofunctional reactants on the physical properties of dimer acid-based polyamides. *Polym Adv Technol*, 17:30-36.
- Chen X, Zhong H, Jia L, Ning J, Tang R, Qiao J, Zhang Z, 2002. Polyamides derived from piperazine and used for hot-melt adhesives; Synthesis and properties. *Int J Adhes*, 22:75-79.
- Chermisinoff NP, 1996. *Polymer characterization laboratory techniques and analysis*, Westwood, New Jersey, USA, p: 17-23.
- Cho SH, Jhon MS, Yuk SH, 1999. Temperature-sensitive swelling behavior of polymer gel composed of poly (N,N-dimethylaminoethyl methacrylate and its copolymers. *Eur Polym J*, 35:1841-1845.
- Cho SH, Jhon MS, Yuk SH, Lee HB, 1997. Temperature-induced phase transition of poly (N,N- dimethylaminoethyl methacrylate-co-acrylamide). *J Polym Sci B: Polym Phys*, 35(4):595-598.
- Deng Y, Fan XD, Waterhouse J, 1999. Synthesis and characterization of soy-based copolyamides with different  $\alpha$ -amino acids. *J Appl Polym Sci*, 73:1081-1088.
- Ebewele RO, 1996. *Polymer Science and Technology*. University of Benin, Nigeria, p. 161.
- Fan XD, Deng Y, Waterhouse J, Pfromm P, 1998. Synthesis and characterization of polyamide resins from soy-based dimer acids and different amides. *J Appl Polym Sci*, 68(2):305-314.
- Guidici R, 1999. Mathematical modeling of an industrial process of nylon-66 polymerization in a two phase flow tubular reactor. *Chem Eng Sci*, 54:3243-3249.
- Hablot E, Donnio B, Bouquey M, Averous A, 2010. Dimer acid-based thermoplastic bio-polyamides: reaction kinetics, properties and structure. *Polymer*, 51(25):5895-5902.
- Heidarian J, Ghasem NM, Ashri M, Daud W, 2004. Study on kinetics of polymerization of dimer fatty acids with ethylenediamine in the presence of catalyst. *J Appl Polym Sci*, 100:85-93.
- Heidarian J, Ghasem NM, Ashri M, Daud W, 2005. Kinetics of polymerization of dimer fatty acid with ethylenediamine after 90% conversion. *J Polym Sci*, 206(6):658-663.
- Heidarian J, Ghasem NM, Daud W, 2003. Kinetic model for polymerization Of dimer fatty acids with ethylenediamine. *J Appl Polym Sci*, 92(4):2504–2513.
- Kale V, Vedanayagam HS, Rao MB, Devi KS, Rao SV, Lakshminarayana G, 1988. Kinetics of reaction of ethylenediamine and dimeric fatty acids. *J Appl Polym Sci*, 36:1517-1524.
- Maitra S, Chakvabarty N, Pramanik J, 2008. Decomposition kinetics of alkaline earth carbonates by integral approximation method. *Ceramica*, 54:268-272.
- Matadi R, Hablot E, Wang K, Bahlouli N, Ahzi S, Averous L, 2011. High Strain rate Behavior of Renewable biocomposites based on dimer fatty acid polyamides and cellulose fibres. *Compos Sci Technol*, 71:674-682.
- Shehap AM, 2008. Thermal and spectroscopic studies of polyvinyl alcohol / carboxy methyl celluloses blends. *Egypt J Solids*, 31(1):75-91.
- Tonbul Y, Yurdakoj K, 2001. Thermogravimetric investigation of the Dehydration ,Turkish bentonite, Turk . *J. Chem*, V25,P33-339.
- Vaudemond R, Hablot E, Matadi R, Ahzi S, Ruch D, Averous L, 2010. Yield behavior of renewable bio-composites of dimer fatty acid-based polyamides with cellulose fibres. *Compos Sci Technol*, 70:525-529.
- Vedanayagam HS, Kale V, 1992. Non-reactive polyamides from C<sub>36</sub> dimer acids: preparation and properties. *Ind Inst Chem Technol*, 33(16):3495-3499.
- Vedanayagam HS, Kale V, Subbarao R, 1992. Kinetics of reaction of C<sub>36</sub> dimeric fatty acids and ethylenediamine in solution. *J Appl Polym Sci*, 45:2245-2248.
- Zhang XZ, Zhang JT, Zhuo RX, Chu CC, 2002. Synthesis and properties of thermosensitive, crown ether incorporated poly (N-isopropylacrylamide) hydrogel. *Polymer*, 43:4823-4827.