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KINETICS STUDY OF THE REACTION OF HYDROGENATED DIMER FATTY ACID C36 WITH 1,7 DIAMINOHEPTANE : DETERMINATION OF THERMODYNAMIC CONSTANTS

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ABSTRACT

Kinetic studies were carried out on the reaction between 1, 7 diamino heptane and hydrogenated C36 dimer fatty acid in melt phase. The reaction was performed at 110, 130, 135, 140, and 150 °C and was followed by determining the acid number of the reactant acid. The polyamidation reaction was found to be of overall second order with an activation energy of 44.0 kJ/mol up to78, 82, 76, 75, 74 % conversion at 110, 130, 135, 140, 150 °C and after the former conversions the reaction will become third order. The degree of polymerization, number average molecular weight, and weight average molecular weight have been calculated during different times. The relationship between degree of polymerization, number average molecular weight and weight average molecular weight with time is linear until (78, 82, 76, 75, 74)% conversion at (110, 130, 135, 140, 150 °C). The kinetics of degradation was carried out by the use of thermal analysis TGA, thermodynamic and equilibrium constants of degradation have been determined. The kinetics of degradation was found to be of overall second order. It was assured of the structure of resulting poly amide by use infra-red spectroscopy.

Keywords: *Kinetic, Thermodynamic Constants, Dimer Acid.*

1. INTRODUCTION

Fatty polyamides are condensation products of di- and polyfunctional amines and di- and polybasic fatty acids[1]. The latter are obtained by the polymerization of unsaturated fatty acids or their esters. Fatty polyamides can be broadly classified into two categories: un-reactive and reactive. The un- 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. Un -reactive polyamides are mostly solids and are used in the printing ink industry, thermo setting, adhesives [2]. The reactive polyamides are mostly liquid and are used in the surface coatings, adhesives industry[3-4]. Dimer acid-based polyamides were prepared due to their singular molecular structure based on their dimer acid relatively good performance [5-6]. Much of the literatures on fatty polyamide preparation are patented [1-2,7].Un -reactive polyamides were prepared by reacting a mixture comprising of polymeric fatty acids, diamines such as ethylene diamine and hexamethylene diamine and an aliphatic monobasic acid or amine, to obtain a product desired, 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

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flexographic inks, adhesives and overprint varnishes [8]. Renewable biocomposites of dimer fatty acid – based polyamides with cellusoe fibers were prepared and studied their thermal, physical, mechanical properties and yield behaviour and high strain rate behaviour [9-11]. 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 reactants. Acetic acid, oleic acid and propyl amine were used as monofunctional reactants [12]. Much of the literature has been reported on the kinetics of this reaction such as nylon-6 and nylon-6, 6 [13] and reaction of dimeric fatty acids $C_{36}$with Ethylenediamineat (124, 130, 145, 160, 174, 190) ^{o}C [14], as well as the reaction between ethylenediamine and dimer fatty acids in benzyl alcohol solution at (160 – 190) ^{o}C [15]. 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 kinetics [16]. A generally applicable stoichiometric and kinetic model was developed for the polymerization of dimer fatty acid with ethylene diamine in melt phase in the presence of phosphoric acid as catalyst at (132-202) ^{o}C [17]. The kinetics of the reaction between ethylene diamine and dimeric fatty acids was studied in melt phase in the range of (162-202) ^{o}C above 90% conversion [18]. Thermal analysis refers to a variety of techniques in which a property of a sample is continuously measured 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[19]. 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 are: thermo gravimetric analysis TGA. By TGA a small amount of the sample is weighed and put in the oven of the TGA apparatus, then the continuous change of mass with temperature under fixed pressure is recorded in the presence of nitrogen. The temperature of sample is gradually increased. One of the applications of TGA is study the kinetics of degradation, But not only the kinetics of this reaction in melt phase for preparing dimer acid-based polyamides with 1, 7 diamino heptane, but also kinetics of degradation of polyamide by use TGA and determination of thermodynamic constants have not been reported by any work. In our work we will study kinetics of this reaction in melt phase for preparing dimer acid-based polyamides with 1, 7 diamino heptane, and we will apply technique of TGA for kinetics of the degradation and determination thermodynamic constants.

2. EXPERIMENTAL

2.1. MATERIALS

Hydrogenated dimer fatty acid C_{36} was from Sigma – Aldrich and was 97% pure and had density 0.95 g / ml , while 1, 7diamino heptane is colorless solidified mass, it was laboratory reagent grade having purity of above 98% as determined by titration with standard acids and had melting point 26-29 $^{\circ}$C. All other materials were reagent grade.

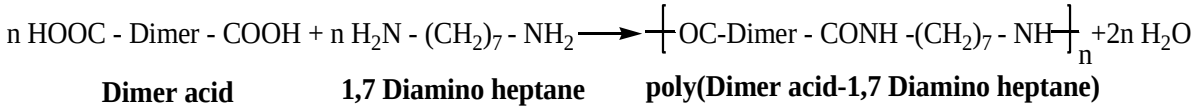
2.2. METHOD

A one liter 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 1, 7 diamino

heptane was added within 2 min, and the heating was regulated to get the desired temperature within 15 minutes. The polyamidation reaction was carried out at five different temperatures in the range of 110-150°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 was finished the kinetics of degradation for the result polyamide were carried out by the use of thermal analysis TGA. Thermodynamic constants for degradation were determined by use thermal analysis TGA and infra-red spectroscopy for determination of resulting compound structure.

2.3. PREPARITION OF POLY (HYDROGENATED DIMER FATTY ACID C_{36} WITH 1, 7 DIAMINO HEPTANE)

Polyamide were prepared from hydrogenated dimer fatty acid C_{36} and 1, 7 diamino heptane as in following equations:



Dimer acid **1,7 Diamino heptane** **poly(Dimer acid-1,7 Diamino heptane)**

2.6. THE EQUATION OF KINETICS REACTION FOR SECOND ORDER

The following equation is used for the second order kinetics:

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

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

If A_{vo} and A_v 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, by acid number equation we can calculate C_A,C_{A0} .

$$A_v = \frac{(V_2 - V_1)(0.0561)(1000)N}{W} \qquad (2)$$

where: W= 1g = 10^3 mg

$$A_v = \frac{(V_2 - V_1)N56.1}{10^3}$$

$$A_v 10^3 = (V_2 - V_1)N56.1$$

$$N(V_2 - V_1) = NV = \frac{(A_v)10^3}{56.1}$$

$$C_A = NV = \frac{(A_v)10^3}{56.1}$$

then C_{Ao} and C_A can be expressed as:

$$CA_0 = \frac{10^3(Av)_0}{56.1} \quad , \quad CA = \frac{10^3(Av)}{56.1}$$

Hence eq. (1) can be written as

$$\frac{1}{A_V} - \frac{1}{A_{V_0}} = \frac{kt}{0.0561} \qquad (3)$$

2.5. THE RELATIONSHIP BETWEEN REACTION RATE CONSTANT AND TEMPERATURE

The relationship is given by Arrhenius equation:

$$k = A\exp^{-E_a/RT_s} \qquad (4)$$

where k = reaction rate constant [$(mol)^{1-n}(time)^{-1}$], T= absolute temperature, n= order of reaction, A: pre-exponential factor $(mol)^{1-n}(time)^{-1}$, E = activation energy (k J/ mol) .

2.6. DETERMINATION OF DEGREE OF CONVERSION:

The degree of conversion [20] is determined according to the following equation:

$$P = \frac{A_{v_0} - A_v}{A_{v_0}} \times 100 \quad (5)$$

Where:

Av_0 : the acid number in the time t_0 (before reaction)

A_v : the acid number in the time t

The acid number A_v is given by the weight of KOH in mg required to neutralize 1g of substance.

2.7. DETERMINATION OF NUMBER AND WEIGHT AVERAGES OF MOLECULAR WEIGHT

The number average of molecular weight Mn [20] is determined according to the following equation:

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

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

M_0:the molecular weight for monomer

P:conversion degree

Where the weight average of molecular weight Mw [20] is determined according to the following equation:

$$M_w = M_0 X_w \quad (8)$$

$$X_w = \frac{1+P}{1-P} \quad (9)$$

2.8. DETERMINATION OF POLYMERIZATION DEGREE

The polymerization degree [20], is determined and calculated according to the following equation:

$$X_n = M_n/M_0 \quad (10)$$

2.9.THE METHOD OF COATS -REDFERN

The use of thermal analysis in the study of the kinetics of degradation by using the equation of Coats-Redfern [21-22] in the following cases:

For n=1

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

For n#1

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

Where α is the fraction of the sample decomposed at time t , n is the order of the reaction, T is the temperature, A is the pre-exponential factor, Ea is the activation energy, R is the gas constant, and q is the heating rate. This method is an integral method that assumes various orders of reaction and compares the linearity in each case to select the correct order [23].

2.10. THERMODYNAMIC AND EQUILIBRIUM CONSTANTS

The entropy calculated from the equation:

$$\Delta S^* = R\left[\ln[\frac{Ah}{KT_s}\right] \quad (13)$$

Where k and h are the Boltzmann and Planck constants respectively, A is the pre-exponential factor, Ts is the maximum temperature of the loss in the mass of the curve of TGA.

The Gibbs free energy(ΔG) and enthalpy (ΔH) are calculated from the equations :

$$\Delta G^* = \Delta H^* - T_s \Delta S^* \quad (14)$$

$$\Delta H^* = E_a - RT_s \quad (15)$$

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

$$\Delta G^{\circ} = -RT \ln K_{eq} \quad (16)$$

R : gas constant. T : temperature (K). K_{eq}: equilibrium constant

The total equilibrium constant for degradation composed of two step is given with:

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

3. RESULTS AND DISCUSSION

The polyamidation reaction in melt phase was carried out at 110,130,135,140and 150˚C was followed by determining the acid number of the reactant acid at each temperature. The reaction could be followed by the fall in acid number of the reactant acid [14-18].The variation in acid number with time of reaction 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[14-18] on kinetics of other polyamidation reactions and also by observing the nonlinear trend in the fall of acid number with time, it was assumed that the acid number relation with time would be characterized an overall second-order reaction which is first order with respect to both acid and amine group concentration. Since equivalent amounts of the acid and amine were taken initially and since the reaction is homogeneous.

Using eq. (2), a plot of $1/A_v$ vs. time was drawn and was found to fit the equation quite well up to about (78, 82, 76, 75, 74) % conversion at (110,130,135,140,150ºC).

The relationship between acid number, and inverse of acid number with time at studied temperature is shown in the following figures:

This shows that the polyamidation reaction follows second-order kinetics up to last conversion. It has also been reported in the literature [14-18] that the results of the polyamidation reaction 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 to be the 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 equation well as shown in figure 3. Rate constants are shown in table (2).

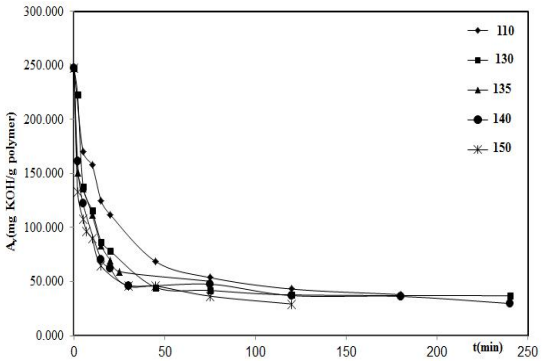


Fig. 1. Changes in Acid value with time at studied temperatures

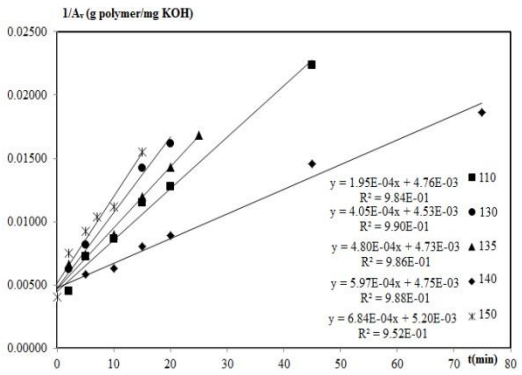


Fig. 2. Changes in (1/Av) with time at studied temperatures

TABLE 1: VARIATION OF ACID VALUE WITH REACTION TIME AT VARIOUS TEMPERATURE

T(°C)	t (min)	A_v (mg KOH /g polymer)	$1/A_v$ (g polymer / mg KOH)	T(°C)	t (min)	A_v (mg KOH /g polymer)	$1/A_v$ (g polymer / mg KOH)
110	0	247.775	0.004036	135	25	59.320	0.01686
	5	170.5	0.005865		75	50.314	0.01988
	10	157.8376	0.006336		120	47.242	0.02117
	15	124.5463	0.008029	140	0	247.775	0.00404
	20	111.9112	0.008936		2	160.943	0.00621
	45	68.56667	0.014584		5	122.140	0.00819
	75	53.71277	0.018618		15	70.345	0.01422
	120	43.15385	0.023173		20	61.875	0.01616
	180	37.97872	0.026331		30	46.321	0.02159
130	0	247.775	0.00404		75	47.632	0.02099
	2	222.827	0.00449		120	37.030	0.02701
	5	138.177	0.00724		180	36.334	0.02752
	10	115.803	0.00864		240	29.777	0.03358
	15	86.881	0.01151	150	0	247.775	0.00404
	20	78.352	0.01276		2	132.868	0.00753
	45	44.701	0.02237		5	108.116	0.00925
	75	41.866	0.02389		7	96.724	0.01034
	120	37.788	0.02646		10	89.521	0.01117
	240	36.952	0.02706		15	64.426	0.01552
135	0	247.775	0.00404		30	45.886	0.02179
	2	151.095	0.00662		45	45.876	0.02180
	5	135.810	0.00736		75	36.571	0.02734
	10	111.753	0.00895		120	29.257	0.03418
	15	83.731	0.01194		75	50.314	0.01988
	20	69.875	0.01431		120	47.242	0.02117

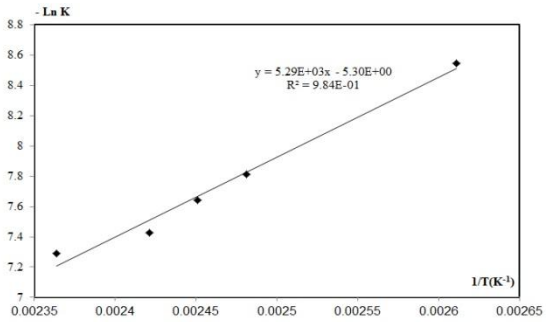


Fig.3.change in -Log K with inverse of temperature

TABLE 2: REACTION RATE CONSTANTS AT VARIOUS TEMPERATURES

T(°C)	T(K)	1/T(K^{-1})	$(con)^{1-n}(time)^{-1}k$
110	383	0.002611	1.95×10^{-4}
130	403	0.002481	4.05×10^{-4}
135	408	0.002451	4.80×10^{-4}
140	413	0.002421	5.97×10^{-4}
150	423	0.002364	6.84×10^{-4}

The activation energy for the second order reaction were calculated from the least square analysis of the data of figure 3 and was found to be 43.981k J/mol.

3.1. MOLECULAR WEIGHTS FOR PREPARED POLYAMIDES

The molecular weight is considered one of the most important properties of polymers that depends on most mechanical and physical properties of polymer besides to other technological usages. Strength and elasticity of polymers is 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 fewer weights relatively. So, dominance of molecular weights during the production is very important. The degree of polymerization, number average molecular weight and weight average molecular weight have been calculated during different times. The tables [3 to 7] show the values of conversion degree, the number average of molecular weight, and polymerization degree through the time of studied temperatures.

TABLE 3: VARIATIONS OF CONVERSION DEGREE, THE NUMBER AVERAGE OF MOLECULAR WEIGHT, AND POLYMERIZATION DEGREE WITH REACTION TIME AT 110°C

T(min)	M_n (g/mole)	M_w (g/mole)	X_n	P%
0	664.230	664.230	1.00	0.000
5	965.276	1266.322	1.45	0.312
10	1042.715	1421.199	1.57	0.363
15	1321.433	1978.635	1.99	0.497
20	1470.627	2277.023	2.21	0.548
45	2400.286	4136.341	3.61	0.723
75	3064.068	5463.907	4.61	0.783
120	3813.787	6963.345	5.74	0.826
180	4333.468	8002.706	6.52	0.847

TABLE 4: VARIATIONS OF CONVERSION DEGREE, THE NUMBER AVERAGE OF MOLECULAR WEIGHT, AND POLYMERIZATION DEGREE WITH REACTION TIME AT 130°C

T(min)	M_n (g/mole)	M_w (g/mole)	X_n	P%
0	664.23	664.23	1	0.000
2	738.598	812.965	1.11	0.101
5	1191.075	1717.920	1.79	0.442
10	1421.206	2178.182	2.14	0.533
15	1894.321	3124.411	2.85	0.649
20	2100.517	3536.803	3.16	0.684
45	3681.772	6699.313	5.54	0.820
75	3931.135	7198.039	5.92	0.831
120	4355.390	8046.550	6.56	0.847
240	4453.863	8243.497	6.71	0.851

TABLE 5: VARIATIONS OF CONVERSION DEGREE, THE NUMBER AVERAGE OF MOLECULAR WEIGHT, AND POLYMERIZATION DEGREE WITH REACTION TIME AT 135°C

T(min)	M_n (g/mole)	M_w (g/mole)	X_n	P%
0	664.230	664.230	1.00	0.000
2	1089.248	1514.266	1.64	0.390
5	1211.837	1759.443	1.82	0.452
10	1472.709	2281.187	2.22	0.549
15	1965.567	3266.905	2.96	0.662
20	2355.328	4046.426	3.55	0.718
25	2774.425	4884.621	4.18	0.761
75	3271.056	5877.882	4.92	0.797
120	3483.748	6303.266	5.24	0.809

TABLE 6: VARIATIONS OF CONVERSION DEGREE, THE NUMBER AVERAGE OF MOLECULAR WEIGHT ,AND POLYMERIZATION DEGREE WITH REACTION TIME AT 140°C

T(min)	M_n (g/mole)	M_w (g/mole)	X_n	P%
0	664.230	664.230	1.00	0.000
2	1022.598	1380.966	1.54	0.350
5	1347.471	2030.711	2.03	0.507
15	2339.612	4014.994	3.52	0.716
20	2659.872	4655.514	4.00	0.750
30	3553.015	6441.801	5.35	0.813
75	3455.226	6246.222	5.20	0.808
120	4444.529	8224.828	6.69	0.851
180	4529.606	8394.982	6.82	0.853
240	5527.058	10389.886	8.32	0.880

TABLE 7: VARIATIONS OF CONVERSION DEGREE, THE NUMBER AVERAGE OF MOLECULAR WEIGHT ,AND POLYMERIZATION DEGREE WITH REACTION TIME AT 150°C

T(min)	M_n (g/mole)	M_w (g/mole)	X_n	P%
0	664.230	664.230	1.00	0.000
2	1238.666	1813.102	1.86	0.464
5	1522.255	2380.281	2.29	0.564
7	1701.536	2738.842	2.56	0.610
10	1838.441	3012.652	2.77	0.639
15	2554.560	4444.891	3.85	0.740
30	3586.695	6509.160	5.40	0.815
45	3587.475	6510.719	5.40	0.815
75	4500.269	8336.308	6.78	0.852
120	5625.336	10586.442	8.47	0.882

The above tables show that the polymerization degree has become 8.47, the number average of molecular weight is 5625.336 and the weight average of molecular degree is 10586.442 at 145°C whereas polymerization degree ranged between 5.20-8.47. The relationship between number average of molecular weight, weight average of molecular weight, and polymerization degree with time is shown in figures (4,5, and 6) where it was found linear (78, 82, 76, 75, 74) % conversion at 110, 130, 135, 140, 150 °C. This is observed in the figures (4, 5 and 6).

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 increases gradually with time, it due to the growth of polymer chains.

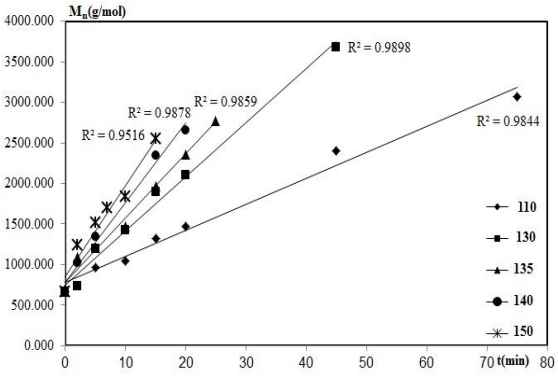


Fig .4. Change in the number average of molecular weight with time at studied temperatures

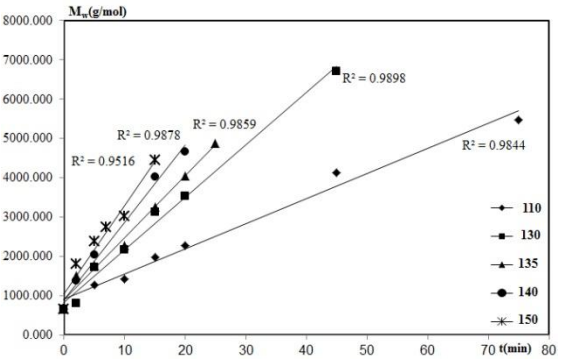


Fig. 5. Change in the number average of molecular weight with time at studied temperatures

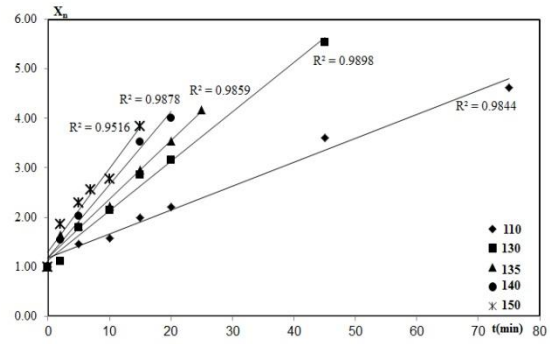


Fig. 6. Change in polymerization degree with time at studied temperatures

3.2. THERMAL STUDY AND KINETIC AND THERMODYNAMIC PARAMETERS:

Since the thermodynamic parameters (ΔH, ΔG, ΔS) can not to obtained 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 final temperature at which degradation finished

(T_{max}): Is the maximum temperature of the loss in the mass, It was determined from the tangent for the TGA curve.

A very small amount of polymer (8.8153 mg) in a small pot of aluminum and placed in oven of the device, the device programmed thermally so that the speed of heating is equal to (10 °C/min) and it was recorded continuous change of the mass for the temperature under a controlled atmosphere in the presence of nitrogen gas. Here the temperature is increased at a programed linear rate. TGA curve shows the loss of weight as a result of the degradation of the sample. Figure (7) illustrate TGA curve of the studied polymer.

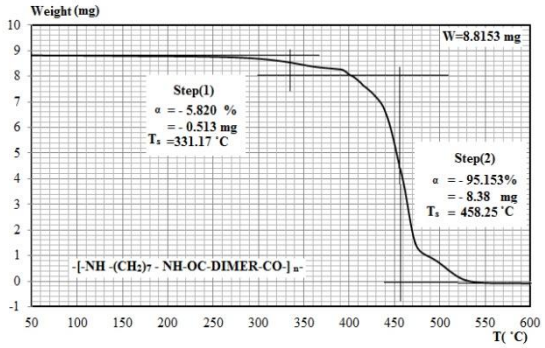


Fig.7. TGA curve of the studied polymer

The activation energy calculated from the slope of the resulting line of the plot of:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \quad \text{vs} \quad 1/T$$

Tables (8) and (9) illustrate values from the slope the result line drawing that presented in figures 8 and 9.

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \text{ vs } 1/T$$

We got the activation energy from the equation $Ea = 2.303mR$, pre-exponential factor determined from the intercept, we notice from the last forms that (R^2 = 0.997) for the degradation of the first stage and (R^2 = 0.9995) for degradation of the second stage in both cases.

TABLES 8: VALUES $\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ VS 1 / T FOR N = 2 STEP (1, A =5.820 %)

T(K)	1/T(K^{-1})	$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$	Slope
463	0.00216	-6.5402	478.665
513	0.001949	-6.62927	
563	0.001776	-6.71005	
613	0.001631	-6.78396	
663	0.001508	-6.85206	

TABLES 9: VALUES $\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ VS 1 / T FOR N = 2 STEP (2 , A = 95.153 %)

T(K)	1/T(K^{-1})	$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$	Slope
703	0.001422	-4.40096	659.998
733	0.001364	-4.43726	
763	0.001311	-4.4721	
793	0.001261	-4.5056	
823	0.001215	-4.53785	

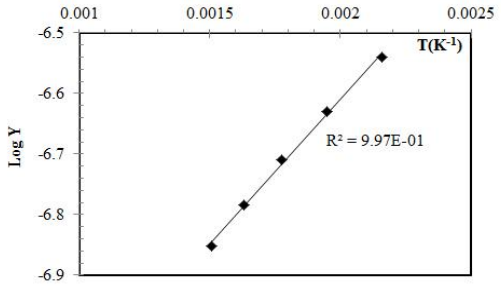


Fig.8.change in Log Y= $\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ with inverse of temperature for step 1.

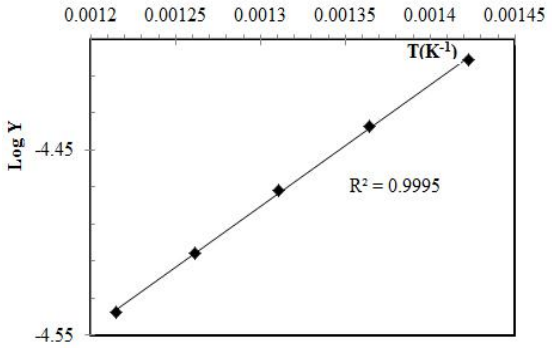


Fig. 9 .change in Log Y= $\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ with inverse of temperature for step 2.

Tables (10) illustrates values of equation (3) for degradation.

TABLES 10: VALUES OF ARRHENIUS EQUATION FOR DEGRADATION

Rate constants	Step(1)	Step(2)
T_s (K)	551.1	731.25
Ea (Kj/mol)	9.165	12.637
mol^{-1} . min^{-1}) (A	6.090	11.439
mol^{-1} . min^{-1}) (k	0.982	1.431

A is the Arrhenius factor determined from the secant intercept on the axis Y.

The activation energy and thermodynamic and equilibrium constants has been calculated according to the last equations, Table (11) illustrate its values.

TABLES 11: VALUES ACTIVATION ENERGY AND THERMODYNAMIC AND EQUILIBRIUM CONSTANTS

Thermodynamic constants	Step(1)	Step(2)	Step(1+2)
T_s (K)	604.17	731.25	-
α (%)	5.820	95.153	-
Ea (Kj/mol)	9.165	12.637	21.802
ΔS (Kj/mol K)	-0.236	-0.232	-0.468
ΔH (Kj/mol)	4.142	6.557	10.699
ΔG (Kj/mol)	146.607	176.315	322.922
(K_{eq})	2.111×10^{-13}	2.541×10^{-13}	2.3161×10^{-13}

Values in the table (the resulting compound is solid) if change of entropy was positive the sample would not be a solid, and thus the reaction occur coercive (the degradation forced to occur by heating) (ΔG positive), we have got very small equilibrium constant due to the reaction is endothermic (the reaction is reversible). However, the reaction is speed when the temperature increases.

3.3. INFRA-RED SPECTRUM

The FT-IR spectrum of dimer acid-based polyamide were obtained using Infra-red device. Polyamide was thoroughly ground with KBr (IR, grade, Merck - Germany) (at a ratio of 1:200) and pressed into a pellet and then the spectrum was recorded. The FT-IR spectrum of dimer acid-based polyamide with 1,7 diamino heptane is shown in fig (10).

Since the reaction is endothermic, and this is illustrated from the positive values of ΔH which is shown in the previous table, as the degradation occur by heating (endothermic), it gives a more regular particles (ΔS negative) , we have noticed its negative.

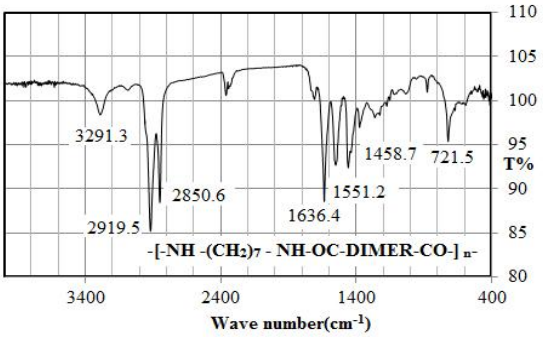


Fig . 10 . infra- Red spectrum for resulted polyamide

Figure (10) illustrates Stretching band at (1636.4cm^{-1}) due to group CO, where the bond N-H have Stretching band at (1551.2 cm^{-1}), the present bands at (721.5 cm^{-1}) due to methylene groups in dimer acid, while the absorption band of N-H appears at a wavelength (3291.3Cm^{-1}) [24-27].

4. CONCLUSION

The polyamidation reaction in melt phase follows an overall second-order kinetics up to78, 82, 76, 75, 74 % conversion at 110, 130, 135, 140, 150 °C with an activation energy of

43.981 k j/ mol. The relationship between the number average of molecular weight, the weight average of molecular weight, and polymerization degree with time is linear until (78, 82, 76, 75, 74) % conversion at (110, 130, 135, 140, 150 °C, the kinetic of degradation was found to be of overall second order.

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دراسة حركية تفاعل الحمض الديميري المهدرج C36مع 7،1 - ثنائي امينو الهبتان و تعيين الثوابت الترموديناميكية

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الملخص:

نفذت الدراسة الحركية على التفاعل بين7،1 - ثنائيامينوالهبتانو الحمض الديميري المهدرج C36 في الحالة المنصهرة ، أنجز التفاعل عند الدرجات (°C150.140.135.130,110) وجرى تعيين قرينة الحموضة للحمض المتفاعل . وقد وجد بأن تفاعل الأميدة كان من المرتبة الثانية مع طاقة تنشيط kJ/mol 44.0 حتى نسب تحول (74,75,76,82,78)%عند درجات حرارة (°C150.140.135.130,110) على الترتيب ثم يتحول التفاعل من المرتبة الثانية إلى المرتبة الثالثة فوق نسب التحول السابقة.

قمنا بتعيين درجة البلمرة وكل من معدل الوزن الجزيئي العددي والوزني خلال أزمنة مختلفة ولوحظ أن علاقة كل من معدل الوزن الجزيئي العددي والوزني و درجة البلمرة مع الزمن علاقة خطية حتى نسب تحول (74,75,76,82,78)% عند درجات حرارة (°C150.140.135.130,110) على الترتيب.

نفذت الدراسة الحركية لتفكك البولي أميد الناتج باستخدام التحليل الحراري (TGA) ، تم تحديد الثوابت الترموديناميكية وثوابت التوازن للتفكك، وجد بأن حركية التفكك تتبع مرتبة ثانية، تم التأكد من بنية البولي أميد الناتج باستخدام مطيافية ماتحت الأحمر.