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Synthesis, characterization and thermal degradation kinetics of Copolyesters

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Abstract The copolymer of lactic acid, ethylene glycol and succinic acid **(cop1)** was synthesized by the condensation process of lactic acid, succinic acid and ethylene glycol. The copolymer was then characterized by FTIR, ^{1}HNMR, ^{13}CNMR, DSC, TGA/DTA; the **(cop1)** was analyzed also for various properties such as acid value, number average molecular weight, etc. The thermal degradation kinetics was investigated for the **(cop1)** by dynamic thermogravimetry, in a nitrogen atmosphere, at the temperature range of 25 °C to 500 °C, at constant nominal heating rates of 10, 15 and 20 °C/min, respectively. Two distinct mass change stages in the thermogravimetric analysis curves indicated that the degradation of **(cop1)** may be attributed to two reactions. The Kissinger, Friedman and Flynn-Ozawa-Wall methods were developed, the corresponding activation energies, frequency factors and reaction orders of the two reactions were determined. We proposed the thermal degradation mechanism of the copolymer.

Keywords: Biodegradable polymer, Thermal degradation; Thermogravimetry; Kinetic analysis.

1. Introduction

In Morocco plastic bags are classified as one of the principal manufacturing products of the synthetic polymer industry; the newspaper economist reported that 120000 Tons of raw materials are used each year (Morocco consumes 24 milliards of plastic bags per year), the incineration has concerned only 1485 Ton between January 2011 and October 2012. The treatment of waste plastic cost 20.000 DH per Ton. The alternative solutions have proposed the law 22.10 to use the biodegradable plastics also an ecotax to finance recycling [1]. Polyesters attract more attention that due to their hydrolysable ester bonds, also aliphatic polyesters are considered to be susceptible to microbial attack; theirs degradation is seen as a two step process: the first is depolymerization. The second is enzymatic hydrolysis, which produces water soluble intermediates that can be assimilated by microbial cells [2]. We need to know more about the aliphatic polyesters; the idea was that knowing the biodegradability, we can also investigate the thermal character, such as the development of heat resistant polymers [3], thermal stabilization of polymers [4,5], and the characterization of high temperature composites for aircraft and aerospace usage [3]. It is evident that thermal degradation may practice serious damage to any polymeric material and can lead to the loss of functionality of the structure. Furthermore a study of the thermal degradation kinetics can provide useful information for the optimization of the processing and use conditions of polymeric materials. The use of TGA/DTA for the determination of kinetic parameters has raised broad interest during recent years. Moreover, the possibility of using different thermal histories can provide further informations on the kinetic nature of the degradation process. Isothermal or dynamic TGA tests at constant heating rate can be used to study the thermal decomposition of polymeric materials, such as aliphatic polyester. Mathematical models of thermal decomposition reactions make possible the understanding of the whole process and the quantitative conclusions are useful for practical applications from apparent kinetic parameter. This paper describes the synthesis and the thermal degradation kinetics of copolymer (lactic acid, ethylene glycol and succinic acid) (**cop1**) between the room temperature and 500 °C, at constant nominal heating rates of 10, 15 and 20 °C/min, respectively. Two distinct mass change stages in the thermogravimetric analysis curves indicated that the degradation of (**cop1**) may be attributed to two reactions. The Kissinger [6], Friedman [7], and Flynn-Ozawa-Wall [8, 9] methods were developed, the corresponding activation energies, frequency factors and reaction orders of the two reactions were determined.

2. Kinetic methods

The application of dynamic TG methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during polymer in the solid state degradation. Thermal degradation is usually defined in terms of kinetic triplet: the activation energy E_a, pre-exponential factor A and the conversion function f (α) [10].

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \quad (1)$$

Where W_t, W_0, and W_f are time t, initial and final weights of the sample, respectively.

$$\frac{d\alpha}{dt} = k.f(\alpha) \quad (2)$$

With the reaction constant k and f (α) is the function of converting α, the parameter k is dependent on the temperature T according to the Arrhenius law,

$$K(T) = Ae^{-Ea/RT} \quad (3)$$

Where R is the gas constant, A is the pre-exponential factor, and E_a is the activation energy for a reaction, f (α) is usually in the form

$$f(\alpha) = (1-\alpha)^n \quad (4)$$

Where f (α) is proportional to the concentration of no degraded material and n is the order of reaction. If we use equation 1 and equation 2 we obtained

$$\frac{d\alpha}{dt} = Ae^{-Ea/RT}(1-\alpha)^n \quad (5)$$

The isothermal analysis is an experience which the heating rate is constant, $\beta = \frac{dT}{dt}$ and equation (5) can be written as

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-Ea/RT}(1-\alpha)^n \quad (6) \quad \text{and}$$

$$\text{Ln}\left(\frac{(\beta d\alpha / dT)}{\exp(-E_a/RT)}\right) = n\,\text{Ln}(1-\alpha) + \text{Ln}(A) \quad (7)$$

The equation (7) show that plotting $\text{Ln}\left(\frac{(\beta d\alpha / dT)}{\exp(-E_a/RT)}\right)$ against Ln (1-α) should give straight lines and its slope is the reaction order and Ln (A) can be easily determined. Activation energy E_a can be calculated by various methods. The first method, the isoconversional method of Ozawa, Flynn and Wall (OFW) [8,9] is in fact, a "model free" method which assumes that the conversion function f (α) does not change with the alteration of the heating rate for all values of α. It involves the measuring of the temperatures corresponding to fixed values of α from experiments at different heating rates β.

Therefore, plotting Ln (β) against $\frac{1}{T}$ in the form of

$$\text{Ln}(\beta) = \text{Ln}\left(\frac{A\,f(\alpha)}{d\alpha/dT}\right) - \frac{E_a}{R} \quad (8)$$

Should give straight lines and its slope is directly proportional to the activation energy ($\frac{-E_a}{R}$). If the determined activation energy is the same for the various values of α, the existence of a single-step reaction can be concluded with certainty. On the contrary, a change of E_a with increasing degree of conversion is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the OFW. These complications are significant, especially in the case that the total reaction involves competitive mechanisms [11]. The second method is Friedman [7] proposed the use of the logarithm of the conversion rate dα/dt as a function of the reciprocal temperature, in the form of

$$\text{Ln}\left(\frac{d\alpha}{dt}\right) = \text{Ln}[Af(\alpha)] + \left(\frac{-E_a}{R}\right) \quad (9)$$

By plotting $\text{Ln}\left(\frac{d\alpha}{dT}\right)$ against $\frac{1}{T}$, the value of the $\frac{-E_a}{R}$ for a given value of α can be directly obtained.

The third method Activation energy E_a can be calculated by Kissinger's method [6]. Kissinger kinetic equation is the most typical and extensive model that is prevailingly applied to evaluate the kinetics. For the results a line can be drawn through the experimental data from thermal analysis and Kissinger kinetic equation:

$$\mathrm{Ln}\left(\frac{\beta}{T_p^{\,2}}\right) = \left(-\frac{E_a}{R\,T_p}\right) + \mathrm{Ln}\left(\frac{AR}{E_a}\right) \qquad (10)$$

Where β is heating rate (°C/min); A is pre-exponential factor (1/min); E_a is activation energy (KJ/mol); T_p is the temperature corresponding to the inflection point of the thermal degradation curves which correspond to the maximum reaction rate obtained from DTG , R is gas constant (=8.314 J/mol K). Therefore, by plotting Ln $\left(\frac{\beta}{T_p^{\,2}}\right)$ against $\frac{1}{T_p}$, the value of the $\frac{-E_a}{R}$ can be directly obtained.

The activation energy can be determined by Kissinger method without a precise knowledge of the reaction mechanism. The models for thermal activation energy are summarized in table 1.

Table 1. Kinetics methods used

Methods	Equations	Plots	Ref
Friedman	$\mathrm{Ln}\,\frac{d\alpha}{dt} = \mathrm{Ln}\,[Af(\alpha)] + \left(\frac{-E_a}{R}\right)$	$\mathrm{Ln}\left(\frac{d\alpha}{dt}\right)$ against $\frac{1}{T}$	[7]
Kissinger	$\mathrm{Ln}\left(\frac{\beta}{T_p^{\,2}}\right) = \left(-\frac{E_a}{R\,T_p}\right) + \mathrm{Ln}\left(\frac{AR}{E_a}\right)$	$\mathrm{Ln}\left(\frac{\beta}{T_p^{\,2}}\right)$ against $\frac{1}{T_p}$	[6]
Flynn-Wall-Ozawa	$\mathrm{Ln}\,\beta = -\frac{E_a}{RT} + \mathrm{CONST}$	$\mathrm{Ln}(\beta)$ against $\frac{1}{T}$	[8, 9]

3. Experimental

3.1. Materials

Lactic acid, ethylene glycol, succinic acid, toluene, Tin (II) chlorides were purchased from Sigma–Aldrich Chemical Co. All reagents were used as received.

3.2. Synthesis of copolyesters

The copolymer was synthesized using lactic acid, succinic acid and ethylene glycol. Lactic acid (0.01 mol), succinic acid (0.19 mol) and ethylene glycol (0.19 mol) were taken in three-necked round bottom flask and 20 ml of toluene was added. A thermometer was fitted to the neck, a stirrer to the other and Dean Stark was fitted to third neck. The temperature was kept at 115 °C for 7 h to remove water by azeotropie. The organic solvent was extracted and 0.1% of $SnCl_2$was added as a catalyst with constant stirring the temperature was carried out at 240 °C under vacuum for another 5 h. The reaction mixture was dissolved in dichloromethane and precipitate in an excess of ether, the white copolymer was removed by filtration and kept at 60 °C under vacuum for 24 hours.

4. Measurements

4.1. End group analysis

4.1.1 Acid value determination (ASTM D 1639)

Acid number was determined by dissolving 0.37 g of polymeric material in ethanol and was titrated against 0.1 N of standardized KOH (using phenolphthalein as an indicator) until a light pink color of the solution persisted. The acid number was calculated by the following expression:

$$\text{Acid number} = \frac{56.1\ V \times N}{m}.$$

Where V is the volume of KOH solution; N is the normality of the KOH solution; m is the weight of polymeric sample taken [12].

4.1.2 Hydroxyl value determination

A quantity of the copolymer must be exactly weighed between(1 and 2g) placed in a 250 ml flask after 20 ml of the acetylating mixture (1 V acetic anhydride and pyridine 3 V) added, stirring for some time we obtained a complete dissolution of the material. The content was refluxed for 30 min, and solution was cooled at room temperature and 50 ml cold water was added. The free acetic acid was titrated with standard 1N NaOH using phenolphthalein as indicator .The procedure was repeated for blank titration under similar condition.

Hydroxyl value = $\frac{56.1\times N\times(B-A)}{W}$.

N is the KOH normality; A is the Volume of KOH solution used for titration; B is the Volume of KOH solution used for blank titration; W is the weight of Copolymer sample taken.

4.1.3 Number average molecular weight (Mn)

The number average molecular weight was calculated using the following expression:

Number average molecular weight Mn = $\frac{F\times 100}{C}$ with F is the functionality of polymer; C acid value.

Also the number average molecular weight was calculated using the following expression:

Mn = $\frac{10^3 \times W}{N\ (V-V_0)}$.

Where W is the weight of copolymer. N is the titer of a solution of KOH in ethanol.
V is the volume of titrated solution and V_0 is the blank volume of titrated solution respectively.

4.2. IR spectroscopy: The FTIR spectrum of the synthesized copolymer was recorded using FTIR B8400S SHIMADZU between 4000 and 600 cm^{-1} at resolution of 4 cm^{-1}.

4.3. Nuclear magnetic resonance (^1H NMR) : The ^1H NMR spectra of the synthesized copolymer was recorded in UATARS - CRNST – RABAT- MOROCCO using spectrometer BRUKER the solvent used $CDCl_3$ with trifluoroacétic acid and TMS as internal reference.

4.4. Thermal analysis

4.4.1 Calorimetric investigation.

Test calorimetric analysis DSC differential scanning unit are formed by a TA DSC Q20 (United State).
We placed about 10 mg of sample in sealed capsules made of aluminum, and subjected to two scan from - 40 to 200 ° C with a rate of 10 °C/min.

4.4.2 TGA/DTA investigation

Thermogravimetric analysis was carried out with SHIMADZU TGA/DTA. Samples were placed in alumina crucibles, an empty alumina crucible was used as reference, and Samples were heated from room temperature to 500 °C in a 50 ml/min flow of N_2. Nominal heating rates of 10, 15 and 20 °C/min were used, and continuous records of sample temperature, sample weight, its first derivative and heat flow were taken.

5. Results and discussion

5.1 Structural analysis of copolyester

Our experimental work accomplished the synthesis of poly (lactic acid ethylene glycol succinic acid) **(cop1)**, the structure of copolymer is given in **(Figure 1 - 3)**

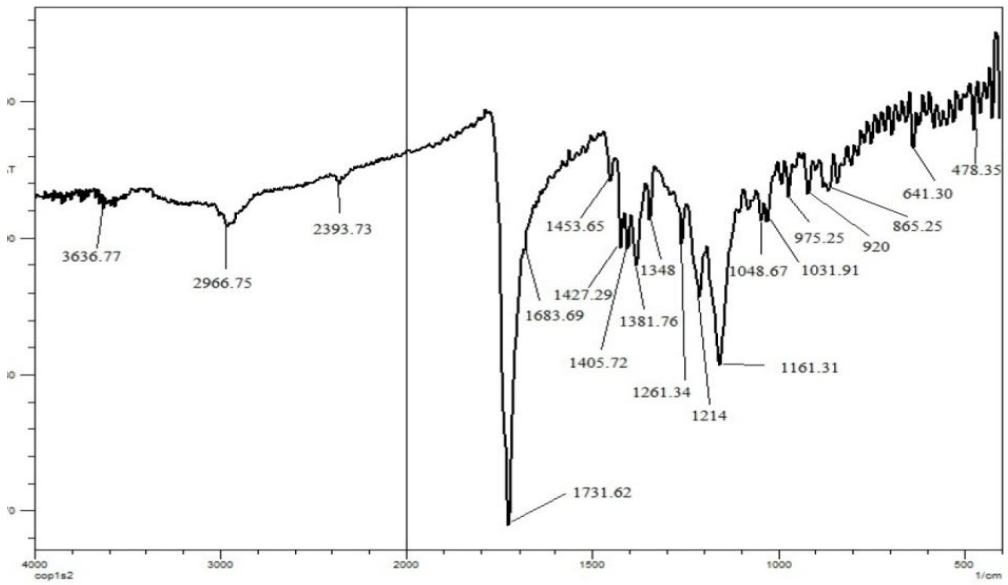


Fig. 1. FTIR spectra of (lactic acid, ethylene glycol and succinic acid) copolymer

Table 2. Absorption band from FTIR spectra of copolymer

	C=O stretching vibrations of the ester carbonyl group	1731.62 cm^{-1}
	C–O–C stretching vibrations of the repeated $–OCH_2CH_2$ units	1161.31 cm^{-1}
(cop1)	–COO- bonds stretching vibrations	1261.34 cm^{-1}
	Terminal hydroxyl groups in the copolymer	3636.77 cm^{-1}
	The C–H stretching bonds	2966.75 cm^{-1}

From FTIR spectra of copolymer in **(Figure1)** the absorption band at 1731.62 cm^{-1} is attributed to the C=O stretching vibrations of the ester carbonyl group. The absorption bands at 1161.31 cm^{-1} and 1261.34 cm^{-1} are attributed to the characteristic C–O–C stretching vibrations of the repeated $–OCH_2CH_2$ units and the -COO- bonds stretching vibrations, respectively. The absorption band at 3636.77 cm^{-1} is assigned to terminal hydroxyl groups in the copolymer. The C–H stretching bonds are at 2966.75 cm^{-1}. All these signals **Table 2** indicate that the **(cop1)** block copolymer may be formed. In order to further confirm the formation of copolymer.

Table 3. Peaks from ^{1}H-NMR spectrum of copolymer

Copolymer	Nature of proton	Peaks
	Methylne proton CH_3–C– of lactic acid unit	1.5 ppm
	Methylene proton on succinic acid unit	2.65 ppm
(cop1)	Methylene proton of EG unit	4.3 ppm
	Proton H–C–O of lactic acid unite	5.1 ppm

An ^{1}H-NMR spectrum is made and shown in **(Figure 2)**. Peaks at 1.5, 2.65, 4.3, 5.1 ppm, the peak at 1.5 ppm is attributed to the methylne proton CH_3–C– of lactic acid unit, the peak at 2.65 ppm is attributed to methylene proton on succinic acid unit, the peak at 4.3 ppm is attributed to the methylene proton of EG unit, the peak at 5.1 ppm is attributed to proton H–C–O of lactic acid unite **Table 3**.

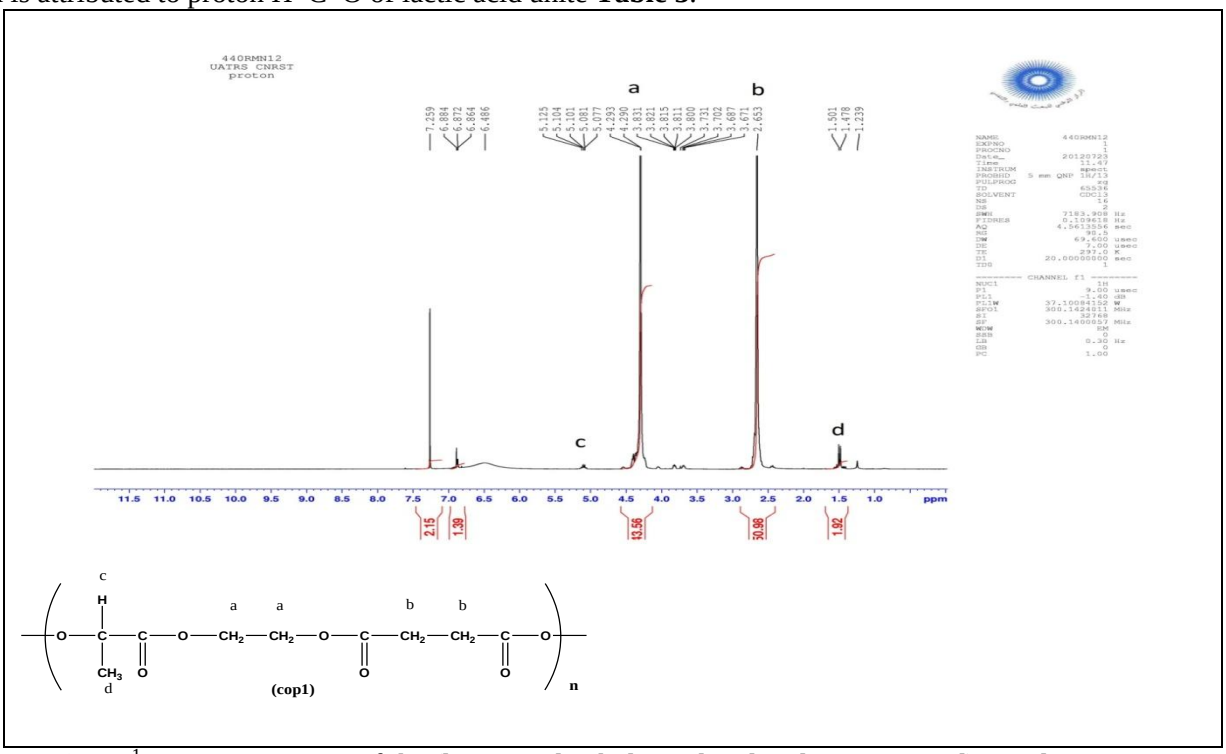


Fig. 2. ^{1}H NMR spectrum of the (lactic acid, ethylene glycol and succinic acid) copolymer

Table 4. Peaks from ^{13}C-NMR spectrum of copolymer

Copolymer	Nature of carbon	Peak
(cop1)	**Methylene carbon of lactic acid unit**	18 ppm
	Methyl carbon of succinic acid unit	28 ppm
	Methylene carbon of ethylene glycol unit and carbon of lactic acid unit	63 ppm
	C=O ester carbonyl	173 ppm
	C=O acid carbonyl	178 ppm

For a third confirmation , an ^{13}C-NMR spectrum is made and shown in **(Figure 3)**, Peaks at 18, 28, 63,173,178 ppm, the peak at 18 ppm is attributed to the methylene carbon of lactic acid unit, the peak at 28 ppm is attributed to methyl carbon of succinic acid unit, the peak at 63 ppm is attributed to methylene carbon of ethylene glycol unit and carbon of lactic acid unit, the peak at 173 ppm is attributed to C=O ester carbonyl and the peak at 178 ppm is attributed to C=O acid carbonyl **Table 4** .

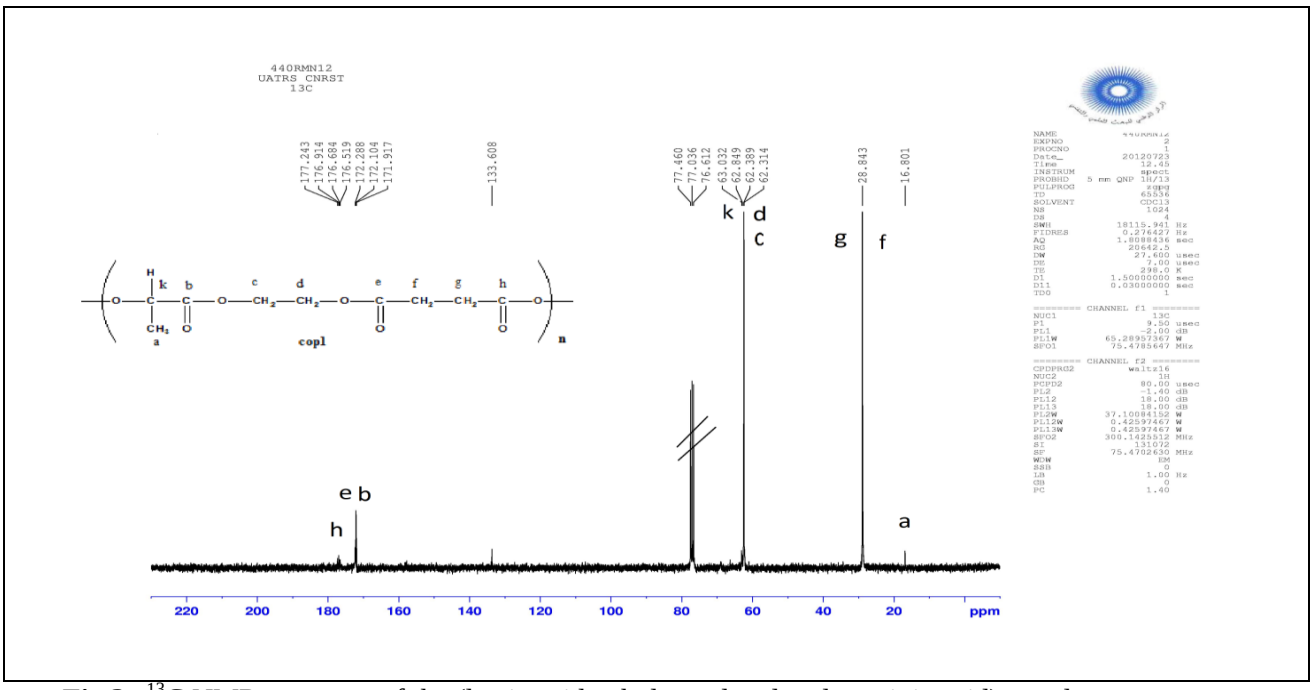


Fig.3. ^{13}C NMR spectrum of the (lactic acid, ethylene glycol and succinic acid) copolymer

5.2 Calorimetric DSC analysis of copolymer

For the differential scanning calorimetry (DSC) analysis results represented in **(Figure 4)** the first run showed a pre-melting at 64.5 °C, the main melting peak at 79.14 °C, the glass transition temperatures of (**cop1)** is more distinguishable in the second scan and it's recorded at - 30 °C, which is further evidence that the copolymer crystallizes slowly. There is no cold-crystallization exotherms, the heat rate of 10 °C/min is faster than the copolymer crystallization, also there is no melting peaks during the second heating run probably that sample is amorphous and most molecules of the copolymer have been destroyed in the first run. The data of the structural and thermal properties of copolyester prepared are summarized in **Table 5**.

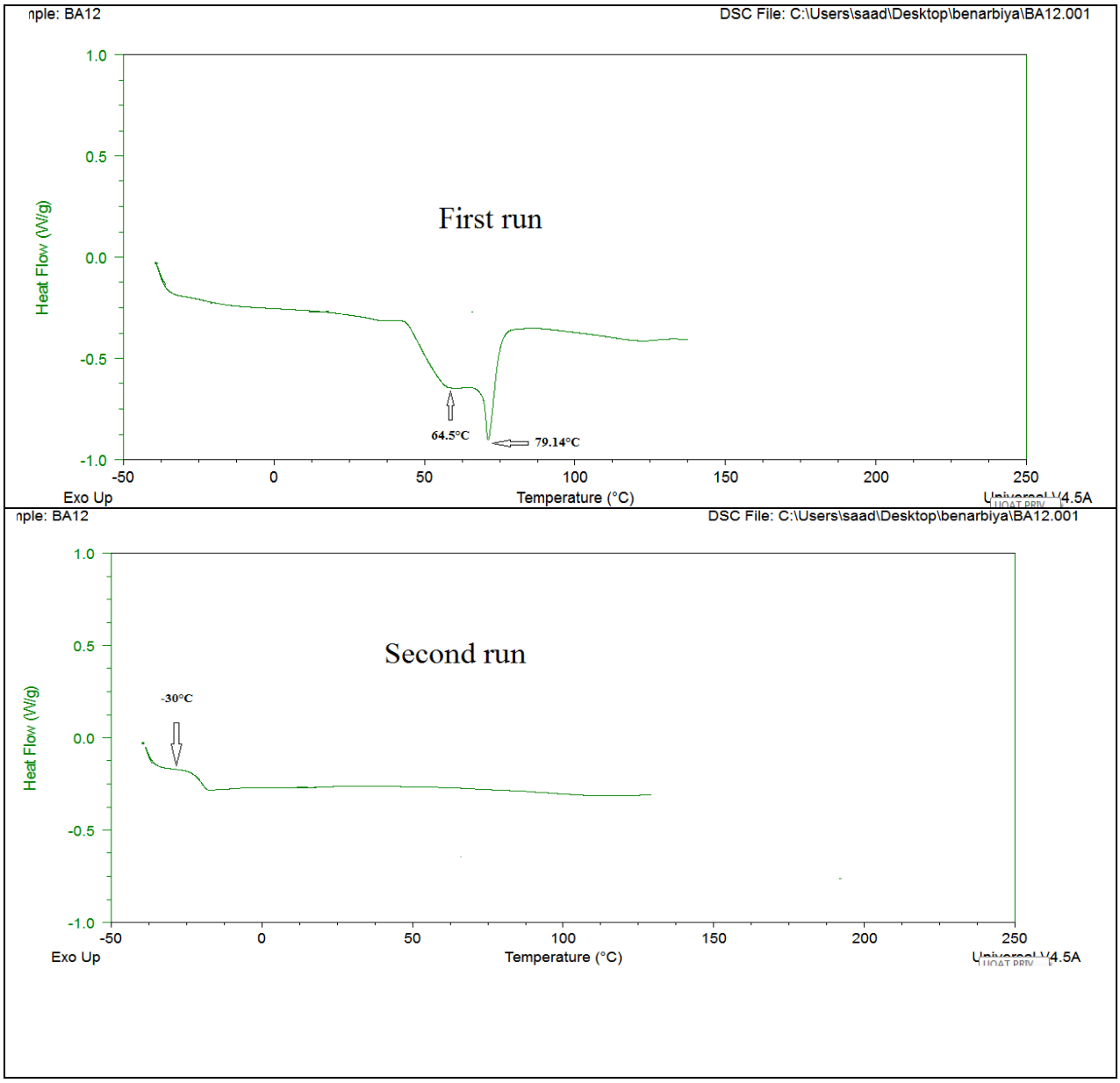


Fig. 4. Differential scanning calorimetry (DSC) of the copolymer

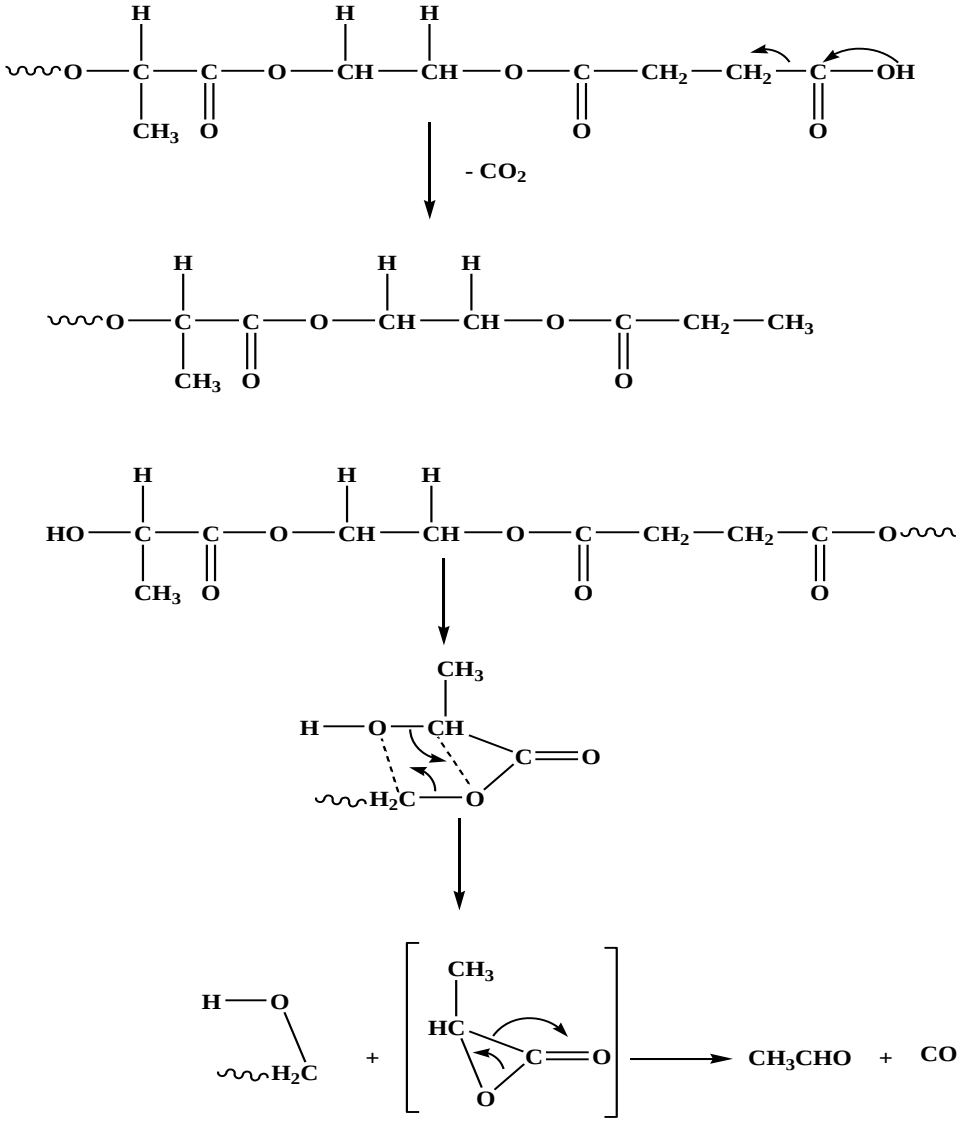
Tg (°C)	T_{pm}(°C)	Tm (°C)	Acid Number	Hydroxyl Number	Molecular Weight
- 30	64.5	79.14	0.2	0.13	≈ 1000g/mol

Table 5. Structure and proprieties of copolyester prepared (* $\mathbf{T_{pm}}$ = pre-melting temperature).

5.3. Thermogravimetric analysis and degradation mechanism

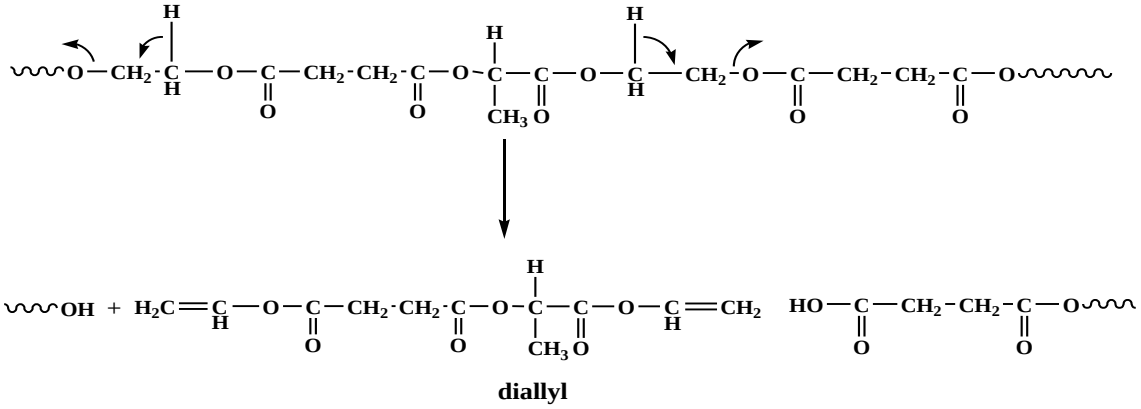
Thermal degradation of the copolymer was studied by determining their mass loss during heating. In **(Figures 5 - 7)** are presented the mass loss (TG mg % and %) and the derivative mass loss (DTG mg/min and %/min) curves. From the thermogravimetric curves TGA % the copolymer under heating rates 10 °C/min **(Figure 6)** it can be seen that the copolymer presents a relatively good thermostability, no significant weight loss occurred until 158.52 °C , and the weight loss (%) 3.35 % was at T= 165 °C. Studies showed that polyethylene succinate is stable until T = 300 °C [12], the succinic acid degrades at a temperature equal at 200 °C and the ethylene glycol degrades at a higher temperature up to 300 °C [13]. The introduction of lactic acid significantly reduces thermal stability in the case of our copolymer. In **(Figure 6)** the variations of instantaneous reaction in DrTGA (% / min) in case of heating rate β = 10 °C/min it is noted that two peak rates can be identified, the first peak at T = 214.11 °C may be caused by small volatile molecules, the catalyst residue, unreacted monomers [14]. The second peak showed rapid deterioration of the copolymer at T = 361.38 °C. An early comprehensive overview

about the mechanism of the thermal decomposition of polyesters was reported by Buxbaum, but only for aromatic polyesters like poly(ethylene terephthalate) [15]. It was shown that esters containing at least one β-hydrogen decompose via a cyclic intermolecular transition state to an olefin and acid end groups, also Tomonaga and coll [16] investigate the random scission and chain-end scission in the thermal degradation of polyethylene and showed that the direct scission and one-step-radical transfer increased with the temperature indicates that β scission occurs on the chain end before the radical transfer because the rate of the β scission becomes faster as the temperature rises. In our case the polyester is aliphatic chain but at least two carbons are nearest which indicate that probability of random scission is very low. Bikiaris and coll investigates the thermal degradation mechanism of an aliphatic polyester poly (propylene succinate) using pyrolysise - gas chromatography- mass spectrometry (Py-GC-MS) and TGA analysis. [17], they conclude that the decomposition of polyester begin by the decomposition of hydroxyl and carboxylic end groups of polyesters, also it was found in similar aliphatic polyesters like polycaprolactone (PCL), at such temperatures a sharp decrease of molecular weight was detected while water, carbon dioxide and 5-hexamoic acid were the main evolved gases [18]. These gases are produced from the decomposition of hydroxyl and carboxylic end groups of polyesters, respectively. These studies showed that for the copolymer **(cop1)** we can propose the mechanism in **(Schemes 1-4)**. The mechanism showed in **(Scheme 1)** is the onset stage of copolymer decomposition as said the decomposition of polyester begin by the decomposition of hydroxyl and carboxylic end groups of polyesters, also L.-T. Lima and coll [19] they reported the thermal degradation of PLA, adapted from McNeill and Leiper, the produced gases are carbone dioxide and monoxide carbone dioxide and Acetaldehyde.



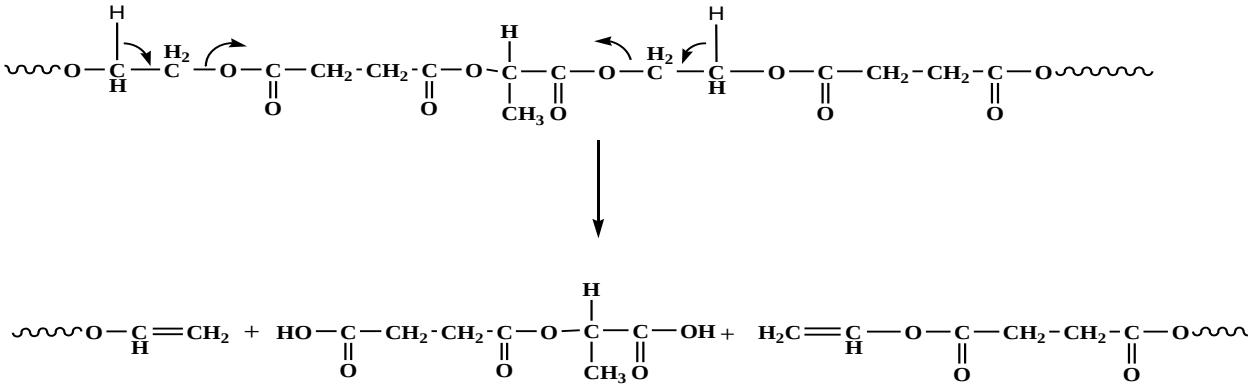
Scheme 1. Proposed mechanism of thermal decomposition of the copolymer. The onset of thermal degradation [17 - 19]

Carboxyl end groups and vinyl groups are formed during decomposition of aliphatic polyesters via β-hydrogen bond scission, which is the main decomposition mechanisms, the two mechanisms in **(Scheme 2 and 3)** are similar [20].



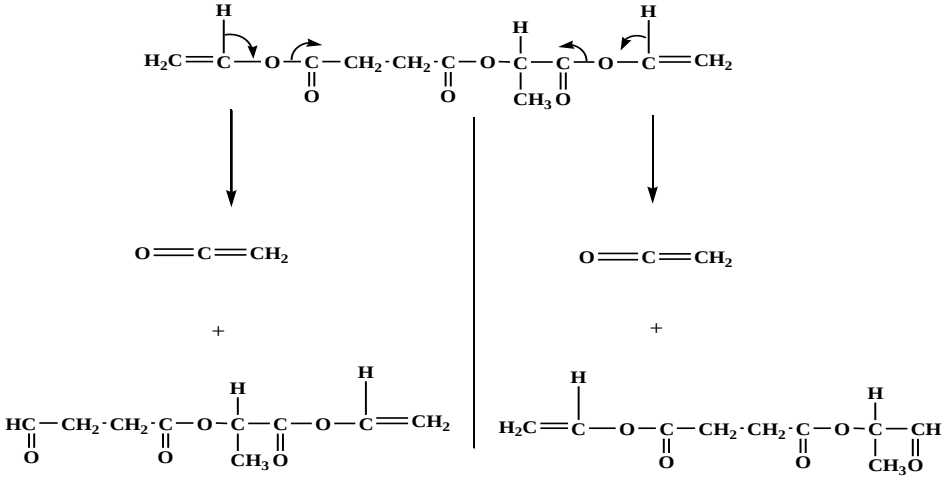
diallyl

Scheme 2.. β-hydrogen bond scission of aliphatic polyesters and the formation of vinyl and carboxyl end groups



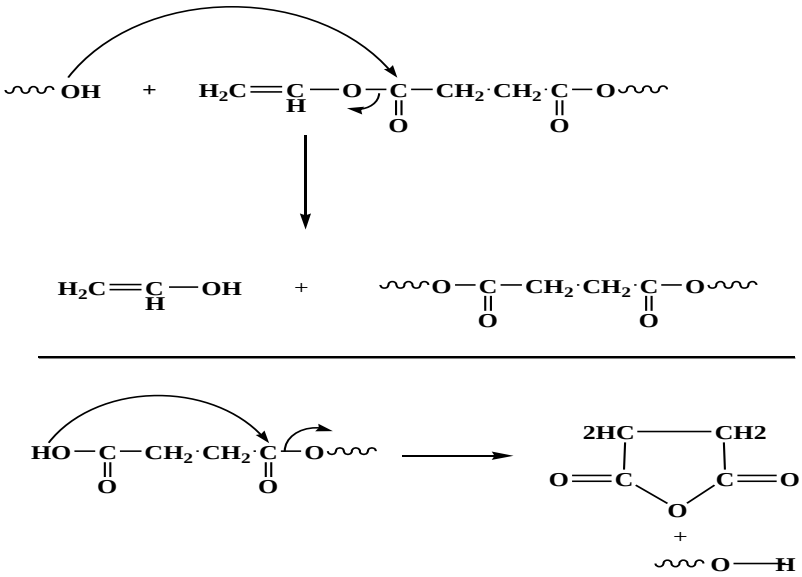
Scheme 3. β-hydrogen bond scission of aliphatic polyesters and the formation of vinyl and carboxyl end groups. The second step of the thermal degradation [20].

The allyl and diallyl are progressively increased with the increase of the decomposition temperature; the α-hydrogen bond scission can also take place and formation of ketene **(Scheme 4)**,

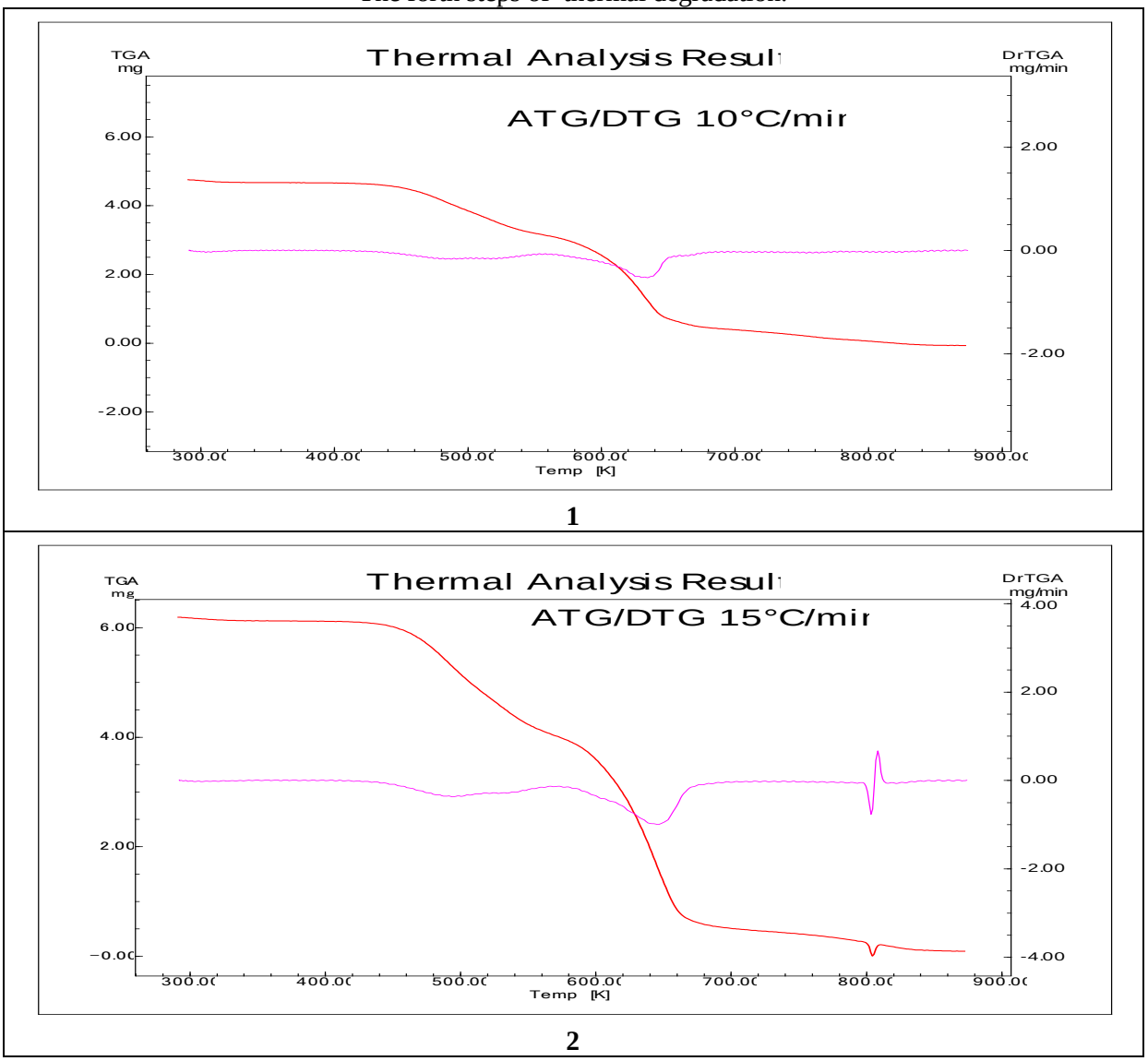


Scheme 4. Proposed mechanism of thermal decomposition of the copolymer. The third steps of the thermal degradation.

Also the intra and inter molecules reactions can also take place and form the anhydrid succinic and ethanol **(Scheme 5).** The third steps of the thermal degradation.



Scheme 5. Proposed mechanism of thermal decomposition of the copolymer.
The forth steps of thermal degradation.



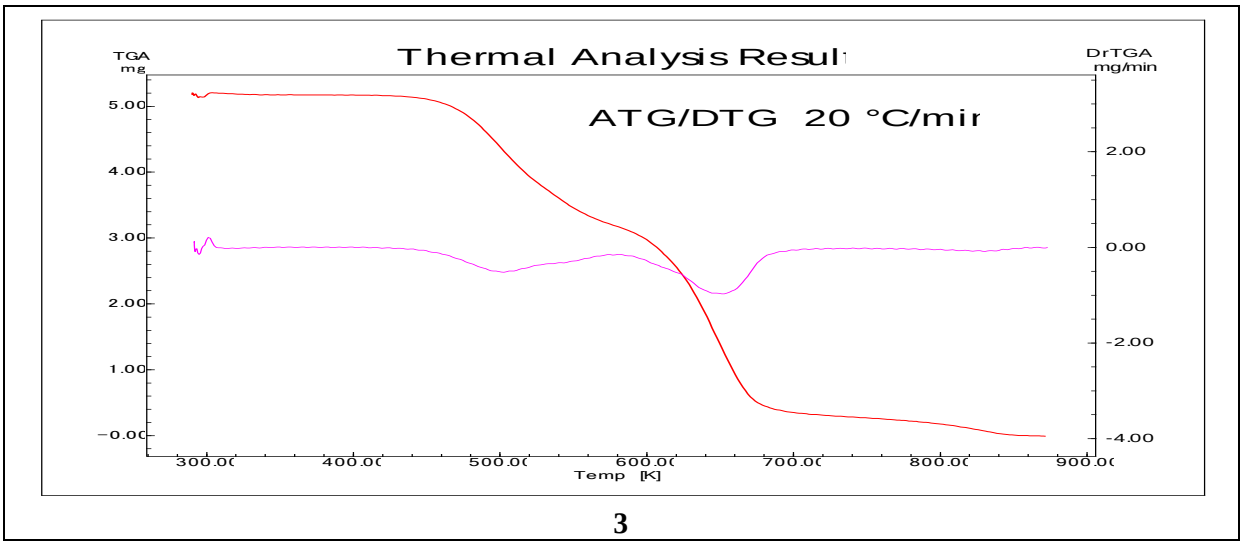


Fig.5. TGA dynamic thermograms of the copolymer at different heating rates β: 10 °C/min; 15 °C/min and 20 °C/min

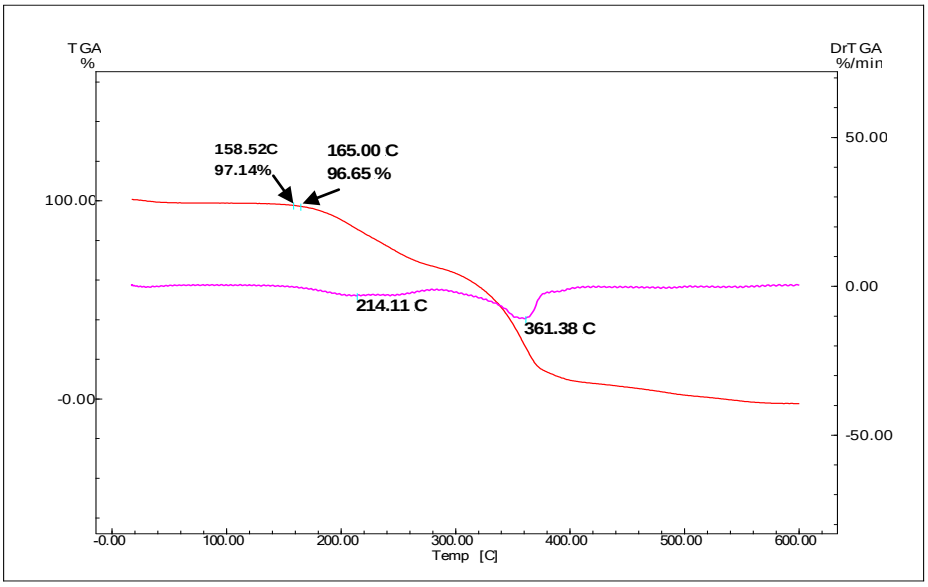


Fig.6. The variations TGA% and DrTGA % of the copolymer under heating rates 10 °C/min

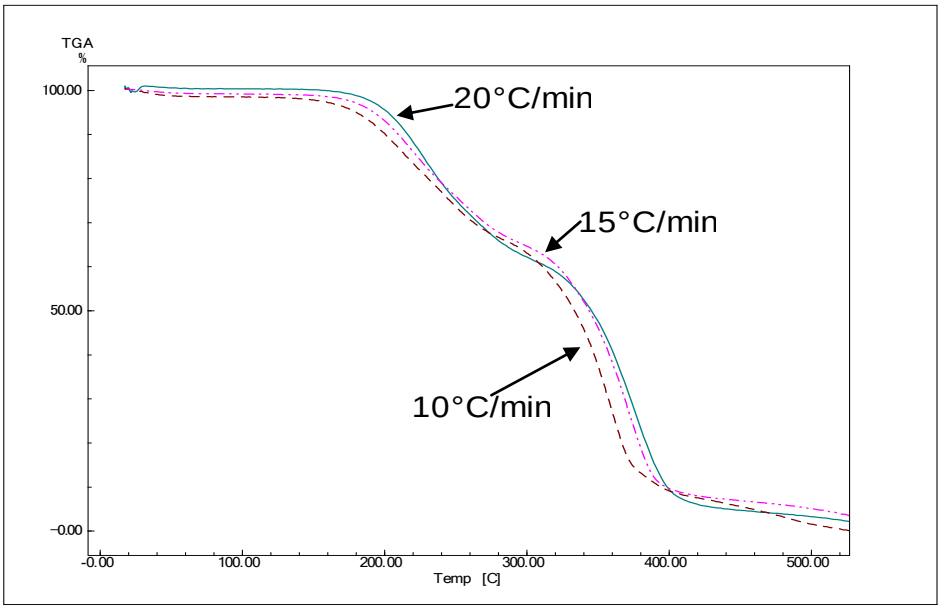


Fig.7. TGA dynamic thermograms of the copolymer at different heating rates β: 10 °C/min; 15 °C/min and 20 °C/min

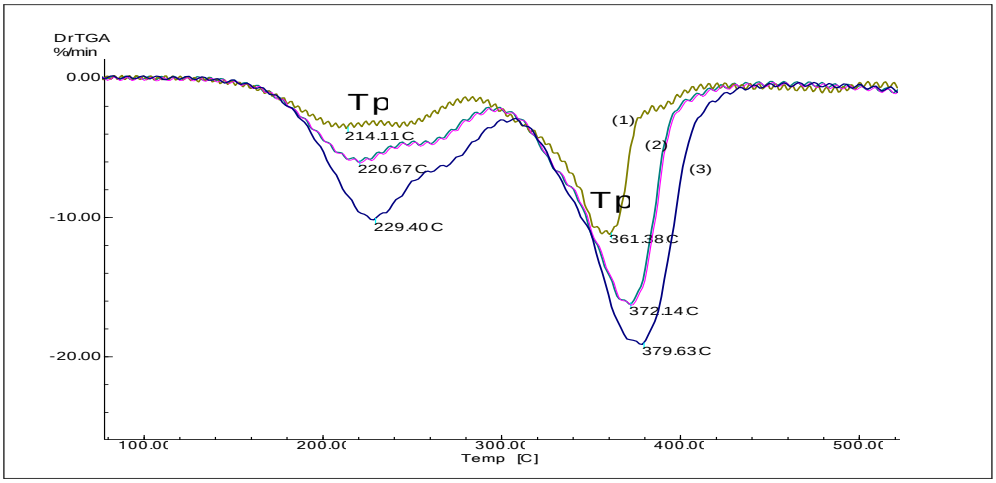


Fig.8. DTG curves of the copolymer at different heating rates β: (1) 10 ◦C/min; (2) 15 ◦C/min; (3) 20 °C/min ; Tp is the most rapidly decomposing temperature used by Kissinger equation.

6. Kinetic analysis of thermal degradation

The DTG for the copolymer under the three heating rates are showed in **(Figure 8)**, it is noted that two peak rates can be identified, for instance, the first peak occurs at about 220.67 °C and weight loss -0.854 mg for a heating rate of 15 °C/min; the second is around 372.14 °C and weight loss -4.439 mg under the same heating rate, this may suggest that two major reactions proceed throughout the experimental conditions. The corresponding fractions α_1 and α_2 caused by the first and second reactions (**Figure 5)** are determined to be (α_1) 0.35 (= 1 – 0.65) and (α_2) 0.65, respectively. The activation energy of degradation of the studied copolymer was estimated using Ozawa, Flynn and Wall (OFW) **Figures (9-10)**, Friedman **Figures (11-12)**, Kissinger **(Figure 13)** methods, all results are presented in **Table 6**.

Table 6. Activation energies of the copolymer using Ozawa and Friedman methods

Conversion α	Activation energy (KJ /mol) Ozawa method	R^2	Activation energy (KJ /mol) Friedman method	R^2
0.05	51.72	0.984	146.11	0.998
0.07	66.97	0.942	175.20	0.983
0.09	78.83	0.988	201.34	0.994
0.1	84.54	0.986	212.58	0.998
0.14	94.22	0.962	240.97	0.986
0.2	220.97	0.934	566.90	0.969
0.3	518.86	0.996	1107.68	0.993
Mean	159.44		378.68	
0.4	168.4	0.338	194.26	0.238
0.5	206.19	0.996	358.89	0.999
0.6	163.36	0.997	296.56	0.997
0.7	160.02	0.999	284.28	0.997
0.8	153.76	0.994	298.39	0.999
0.85	144	0.990	436.74	0.949
Mean	165.95		311.52	

Table 6. Activation energies of the copolymer using Kissinger methods

***** Where α_{max} is the conversion corresponding to the maximum of a differential kinetic curve

Activation energy (KJ/mol) Kissinger method (first reaction)	* α_{max}	R^2	Activation energy (KJ/mol) Kissinger method (second reaction)	*α_{max}	R^2
87.45	0.14	0.986	119.85	0.8	0.999

From the data in **Table 7** The method of Kissinger uses the maximum decomposition temperature (T_p) at which the rate of weight loss is the highest , α_{max} is the conversion corresponding to the maximum of a differential

kinetic curve, for the first and second reaction α_{max} = 0.14 and 0.8.The activation energy was also calculated by the Kissinger method giving 87.45 KJ/mol for the first reaction step with a correlation coefficient of 0.986 and 119.85 KJ/mol for the second reaction step with a correlation coefficient 0.999, These E_a values are in good agreement with those found by Ozawa method **Table 6** , α = 0.14 E_a = 94.22 KJ/mol with a correlation coefficient 0.962 and for α = 0.8 E_a=153.76 KJ/mol with a correlation coefficient 0.994, the little difference between two energies (6.7KJ/mol for the first step and 33.9 KJ/mol for the second step can be explained by a systematic error due to improper integration [21], no values were found to compare with Friedman method, ,in authors opinion, there are two possible reasons that may explain this discrepancy, One is the difference of the molecular weight and molecular weight distribution between the copolymer samples chosen in our research work. The other is the difference of the chain-end structures of the copolymer, which was originated from the polymerisation using $SnCl_2$ [22]. We used the Ozawa result for the determination of reaction order and pre exponential factor for all reaction.

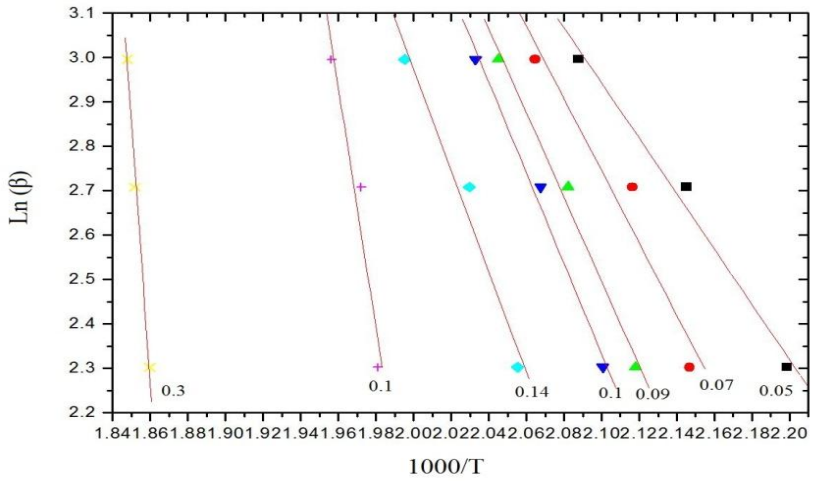


Fig.9. Ozawa plots of the copolymer at fractional extent of reaction: α = 0.05; 0.07; 0.09; 0.1; 0.14; 0.2 and 0.3.

For the determination of the activation energy by using multiple heating rates the above analyzed isoconversional methods are used. Since every isoconversional method has different error, the use of more than one method can give a range of values for the activation energy at every particular value of α, the plots of Ln (β) versus 1000/T of the Ozawa–Flynn–Wall (OFW) method, for **(cop1)** The straight lines fitting the data are showing in **(Figure 9)** for the first reaction step. In **(Figure 10)** the straight lines fitting the data are showing for the second reaction step.

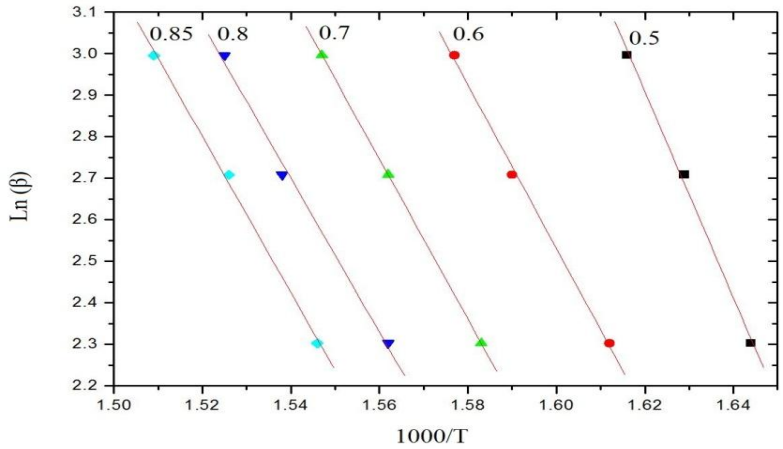


Fig. 10. Ozawa plots of copolymer at fractional extent of reaction: α = 0.5; 0.6; 0.7; 0.8; and 0.85

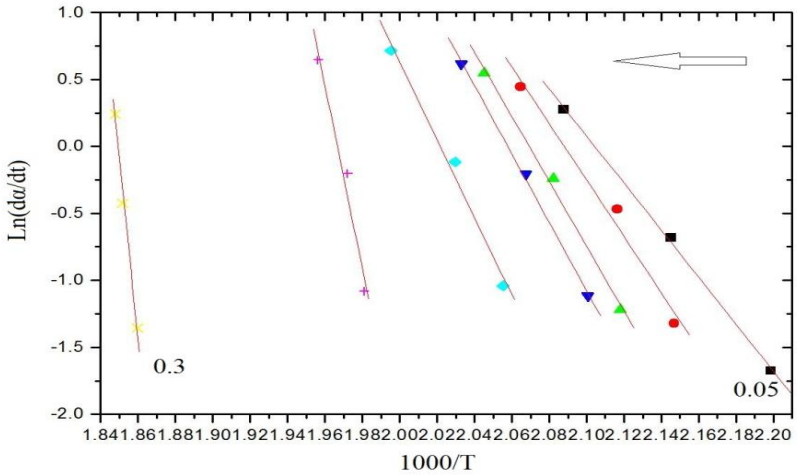


Fig.11. Friedman plots of copolymer at fractional extent of reaction: α = 0.05; 0.07; 0.09; 0.1; 0.14; 0.2 and 0.3

Friedman method was also used by plotting Ln ($\frac{d\alpha}{dt}$) versus $\frac{1000}{T}$ for a constant value and the activation energy was calculated, in **(Figure 11)** the straight lines fitting the data are showing for the first reaction step. In **(Figure 12)** the straight lines fitting the data are showing for the second reaction step.

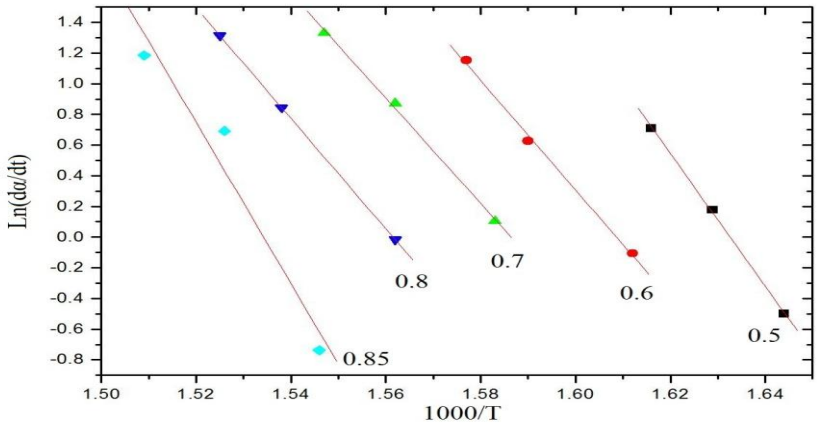


Fig.12. Friedman plots of copolymer at fractional extent of reaction: α = 0.5; 0.6; 0.7; 0.8 and 0.85

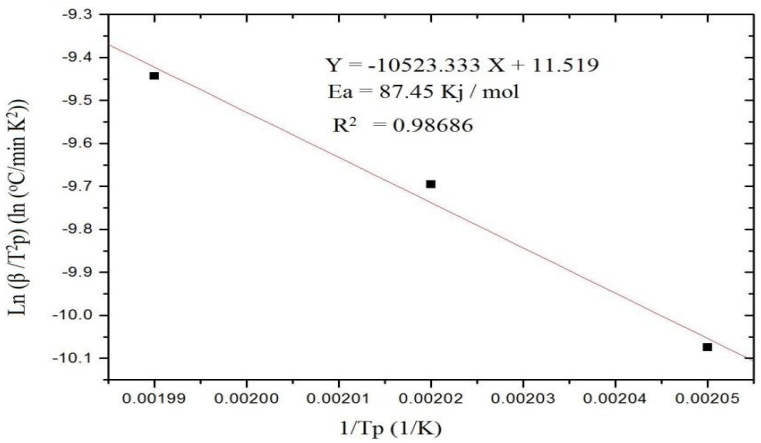


Fig.13. Kissinger plots of copolymer (first reaction)

The terms $\frac{1}{T_p}$ and Ln ($\frac{\beta}{T_p^2}$) could be obtained by DTG results of heating rate **(Figure 8)**. Therefore $\frac{1}{T_p}$ was represented for x axis and Ln ($\frac{\beta}{T_p^2}$) denoted for y axis to draw a **(Figures 13 - 14)**. After three heating rates and three T_p were substituted into Eq (10), a graph and a linear regression equation could be acquired. The activation energy was determined for the first and the second reaction respectively **Table 7**. With 87.45 KJ/mol and 119.85 KJ/mol respectively.

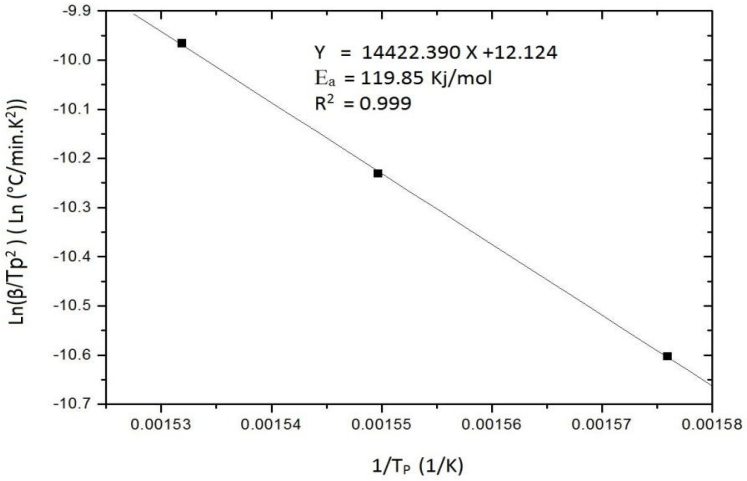


Fig.14. Kissinger plots of copolymer (second reaction)

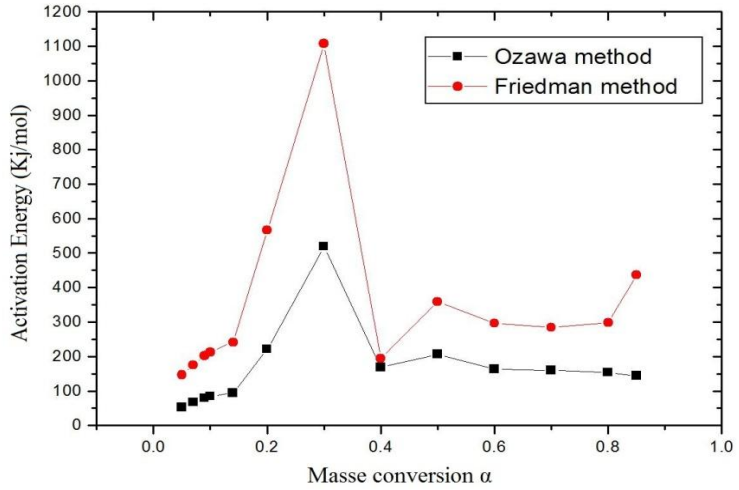


Fig.15. Dependence of the activation energy (E_a) on the mass conversion (α), as calculated with Friedman and OFW methods for the copolymer

The apparent activation energy (E_a) previously determined **Table 6** were evaluated utilizing both the classical Friedman and Ozawa methods, all process is described. It can be seen that there is two important steps **(Figure 15)** the first step when E_a increase and that is when $0.05 \leq \alpha \leq 0.3$; the second step when E_a decrease and became relatively stable and that is when $0.4 \leq \alpha \leq 0.85$, confirmed that there is two kinds of reaction mechanism using two fractions F1 =0.35 and F2 = 0.65.
The low E_a for the first step has, however, been attributed to volatilization of impurities, (small volatile molecules, the residue of the catalyst, monomers unreacted). It is important to note that all authors reported that

the activation energies of the degradation process depend largely on the polymerization methods which determine the nature of end groups. María Angeles and coll [23] prove in their work published in Journal of Analytical and Applied Pyrolysis that while the combustion progresses a carbonaceous residue is slowly forming. This carbonaceous residue limits the diffusion of the decomposed volatile products and, as a consequence, the activation energy increases. The determination of the reaction order for the first reaction step is very complex but our approach use the equation

$$\text{Ln}\ \frac{(\beta \mathrm{d}\alpha / \mathrm{dT})}{\exp\left(-\mathrm{E_a} / \mathrm{RT}\right)} = \text{n Ln (1- α) + Ln (A)} \qquad (7)$$

All the authors have the same results the reaction order concerned the first thermal reaction step for the polyesters is classified as first order its mean n = 1.

If we suppose that n = 1, the equation (7) show that plotting $\text{Ln}\ \frac{(\beta \mathrm{d}\alpha / \mathrm{dT})}{\exp\left(-\mathrm{E_a} / \mathrm{RT}\right)}$ against Ln (1-α) should give straight lines. The activation energy used is the statistic mean first reaction Ozawa method (159.44 KJ/mol, **Table 6**) and the fraction used is between (0.05 and 0.3) that concerned also first reaction for the same case β = 10 °C/min. The same procedure for the second reaction step, the activation energy used is the statistic mean second reaction Ozawa method (165.95 KJ/mol, **Table 3**)and the fraction used is between (0.4 and 0.85) that concerned also the second reaction for the same case β = 10 °C/min. The results indicate that the first decomposition has a reaction order of one **(Figures 16 –17)**, but the second decomposition does not **(Figure 18)**. To determine the reaction order for the second decomposition, the previous equation needs to be modified by taking n≠1. By using Microcal Origin as informatics logiciel and linear fit as application of these logiciel **(Figure 19)** we found that n = 1.84 and Ln(A) = 33.8404, and the pre exponential factor A = 5.10^{14} min^{-1}

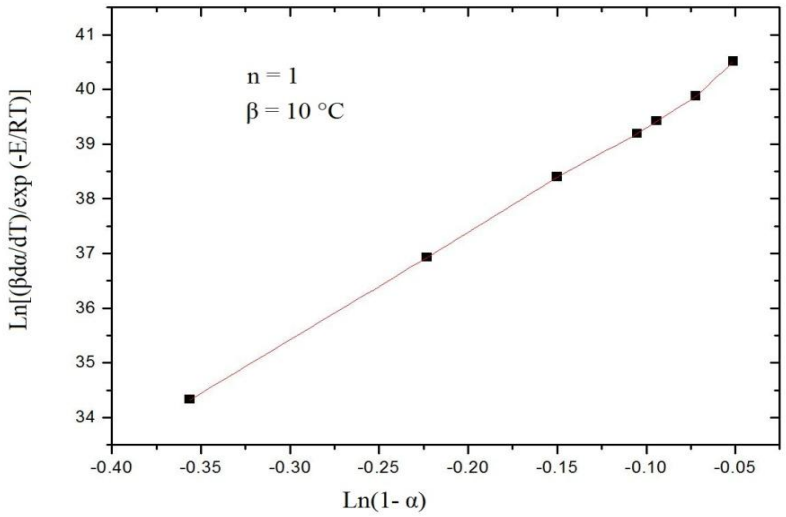


Fig.16. Variations of $\text{Ln}\ \frac{(\beta \mathrm{d}\alpha / \mathrm{dT})}{\exp\left(-\mathrm{E_a} / \mathrm{RT}\right)}$ with Ln (1 - α), β=10 °C/min, for pyrolysis of the copolymer, experimental and correlated results of first reactions [24].

The approach assumes the basic Arrhenius equation:

$$\beta \frac{\mathrm{d}\alpha}{\mathrm{dT}} = \mathrm{A}\ e^{-Ea/RT}\ (1-\alpha)^n \qquad (6)$$

We found that n = 1 by plotting $\beta \frac{\mathrm{d}\alpha}{\mathrm{dT}}$ against $e^{-Ea/RT}(1-\alpha)$ and $0.05 \leq \alpha \leq 0.1$ Should give straight lines and its slope is directly proportional to pre exponential factor A **(Figure 17)** .

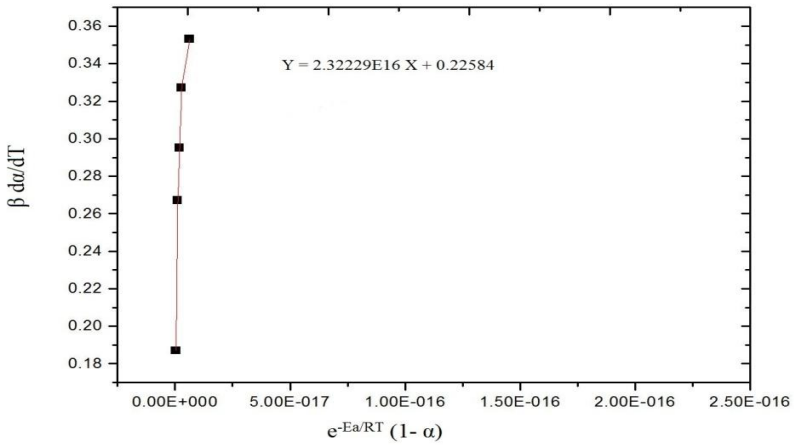


Fig.17. Variations of $\beta \frac{d\alpha}{dT}$ with $e^{-Ea/RT}$ (1- α), β=10 °C/min, for pyrolysis of the copolymer, using Microcal Origin as informatics logiciel and linear fit as application of these logiciel.

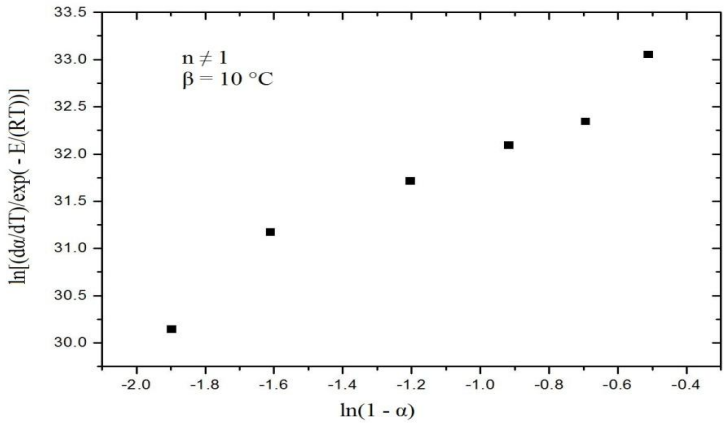


Fig.18. Variations of Ln $\frac{(\beta d\alpha / dT)}{\exp(-E_a / RT)}$ with Ln(1 - α), β=10 °C/min, for pyrolysis of the copolymer, experimental and correlated results of second reactions [24].

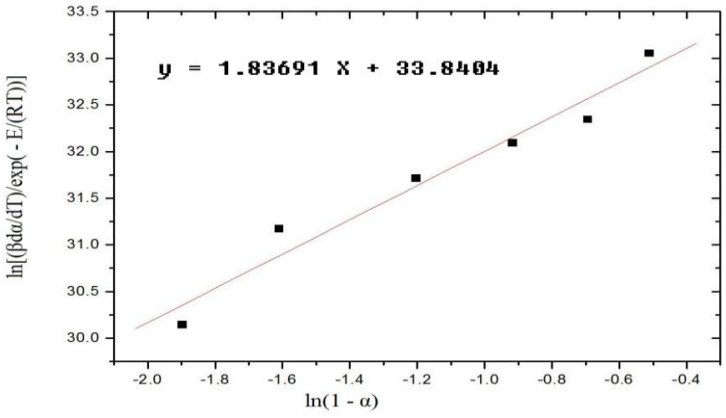


Fig.19. Variations of Ln $\frac{(\beta d\alpha / dT)}{\exp(-E_a / RT)}$ with Ln (1 - α), β=10 °C/min, for pyrolysis of the copolymer, fit linear experimental and correlated results of second reactions [24].

Sample	Fraction contributed by the first reaction	E_a (KJ)	n	Pre-exponential Factor A (min^{-1})	Fraction contributed by the second reaction	E_a (KJ)	n	Pre-exponential factor A (min^{-1})
(Cop1)	0.35	159.44	1	$2.33.10^{16}$	0.65	165.95	1.84	$4.97.10^{14}$

Table 8. Calculated values of fraction contributed, activation energy, reaction order and pre-exponential factor for the two reaction mechanisms of the copolymer

Conclusion

In these work we synthesized an aliphatic and biodegradable polyesters (due to the hydrolysable ester bonds) the copolymer of lactic acid, ethylene glycol and succinic acid (**cop1**) with molecular weight ≈1000g/mol, the copolymer presents pre-melting temperature at 64.5 °C and melting at 79.14 °C while the glace transition at -30 °C. According to TG and DTG analysis it was found that mass loss is accomplished in two stages. The Kissinger, Friedman and Flynn-Ozawa-Wall methods were developed, the activation energies for all values of α, were determined, from the dependence of activation energy on the α value, it was identified the existence of two regions for E values: the first step when E_a increase and that is when $0.05 \leq \alpha \leq 0.3$; the second step when E_a decrease and became relatively stable and that is when $0.4 \leq \alpha \leq 0.85$, confirmed that there is two kinds of reaction mechanism using two fractions, fraction contributed by the first reaction F1 = 0.35 and fraction contributed by the second reaction F2 = 0.65. The method of Kissinger uses the maximum decomposition temperature (Tp) are in good agreement with those found by Ozawa method , no values were found to compare with Friedman method, it is useful to use more than two methods. The Ozawa results for the determination of reaction order and factor preexpenentiel were used.

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