Indian Journal of Chemistry
Vol. 63, September 2024, pp. 860-867
DOI: 10.56042/ijc.v63i9.10604

Thermogravimetric analysis of 2,6-diaminopyridine substituted polymers using green conditions and conventional method

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Received 22 April 2024; accepted (revised) 30 August 2024

Polyamides have been synthesised by a modified phosphorylation method using 2,6-diaminopyridine with diacids such as citraconic acid, succinic acid and phthalic acid. Reaction has been carried out with NMP/Pyridine mixture containing 4% LiCl using the following conditions: Higashi to increase viscosity and thermal stability, reported by the authors. In the present study we carried out the synthesis under green conditions ionic liquid and microwave combined with ionic liquid and the results have been compared. Thermogravimetric analysis of synthesized polymers have been performed in the temperature range 30 to 900°C. Thermogravimetric data have been used to calculate activation energies and compared with other integral and differential methods like Friedmann, Freeman-Carroll, Coats-Redfern, Chang, Sharp Wentworth. Kinetic parameters - Gibb's free energy, entropy and enthalpy have been determined for all polyamides synthesized using microwave assisted ionic liquid method employing Coats-Redfern method. Regression analysis has been carried out for all the three polyamides for all the stages of decomposition which involves seven different kinetic models. The limiting oxygen index has been calculated and the fire-retardant properties have been noted. This result is compared with all known methods.

Keywords: 2,6-Diaminopyridine, Succinic acid, Phthalic acid, Citraconic acid, Energy of activation, Thermogravimetry, Limiting Oxygen Index (LOI), Regression analysis, Kinetic models

Amides have unique characteristics because of the conjugation link between the lone-pair of nitrogen and carbonyl bond and it leads to physico-chemical properties like inflexibility and thermal stability. Bajpai *et al.*[1] reported the unsaturated polyamides based on glutaconic acid where an unsaturated double bond and amide will be present in polyamides as functional groups.

Majority of the polyamides prepared at a higher ratio of diamine concentration may have amino terminated group. The double bond and terminated amino group will be highly useful in post curing reaction for number of industrial applications[2–4]. In organic synthesis ILs play a vital role as green alternative solvent. Only a small amount of ILs are employed to increase the dielectric constant of an otherwise non polar solvent medium. Microwave assisted synthesis of polyamides provides clean synthesis with the advantages of higher productivity, greater selectivity, superior reaction rates, and cost-effective synthesis of large number of polyamides. Because of these advantages, many chemists opted microwave assisted synthesis over conventional heating techniques. Microwave coupled ILs synthesis of polyamides surpassed the advantages of individual microwave assisted green synthesis and ILs assisted green synthesis. With a view to synthesise polyamides with high solubility, thermal stability and better processability several attempts have been made to modify the method of preparation[5-8].

In the present work, experiments was carried out by modified phosphorylation method, MW assisted IL method and IL method and the results compared. Viscosity of the polyamides increased from 0.22 to 0.71. The paper also reports on the use of TGA and DSC methods for kinetic studies. Various integral and differential methods were used to evaluate the energy of activation and kinetic parameters like G, H, S was calculated using Coats and Redfern method of approximation taking n=1. Regression analysis was also carried out for various kinetic models.

Experimental Section

Preparation of Polymers

Experiment 1

In the present work the modified phosphorylation method was employed, and Higashi's conditions were adopted to synthesise polymers. A combination of 2,6-diaminopyridine (0.005mol), diacid (0.005mol) (such as phthalic acid, succinic acid, and citraconic acid), and triphenyl phosphite (0.01 mol) was mixed with 65 mL of NMP solution ,Pyridine 10 mL, LiCl (l g), and $CaCl_2$ (3 g). To get a viscous solution, the reaction mixture was heated to 110°C for four hours while being stirred. The viscous solution thus obtained was added to heated methanol in order to precipitate polymers. After filtering, the final product was cleaned with dil.HCl, an aqueous solution of Na_2CO_3, water and methanol. The resultant polymers were dehydrated in vacuum at 100°C over P_2O_5 for 24 h[9,10].

Experiment 2

Microwave apparatus (Samsung microwave oven (2,450 MHz, 900 W)) was used for polycondensation. In a porcelain dish 0.005 mol of dicarboxylic acid and 0.005 mol of diamine were dissolved in 1,3 dipropylimidazolium bromide under heating. The entire mixture was covered with a watch glass. The reaction mixture was subjected to 530 W of microwave radiation for 60 s. The polymer got precipitated when 20 mL of methanol were added to the reaction mixture.

Experiment 3

In a 25 mL round bottom flask 0.005 mol of dicarboxylic acid and 0.005 mol of diamine were dissolved in 1,3 dipropylimidazolium bromide (0.2 g). 0.13 mL (4.88×10^{-4}mol) of TPP was then added and the reaction mixture was heated at 110°C for 5 h with continuous stirring. Finally methanol is added to precipitate the polymer.

Thermogravimetry study was performed on the synthesised polymers employing microwave assisted IL's between 40 and 800°C. The plot of the synthetic polyamides' % weight loss against temperature was used to determine the activation energy. The thermograph was analysed to find the significant decomposition temperature, and it was designated as the starting decomposition temperature. Applying several methodologies[11-15], the activation sequence and energy for the most significant phases in the decomposition reaction were established. Friedmann Technique[16,17], Chang[18], Sharp-Wentworth[19], Freeman and Carroll[20] and Coats and Redfern[21] were used to obtain the results[22-24].

Chang Technique

$\ln(d\alpha /dt)/ (1- \alpha)^n = \ln(Z) - Ea /RT$

[$\ln(d\alpha\ dt)/(1- \alpha)^n$ *versus* 1/T] will yield a straight line with slope and intercept (-Ea/R) & ln(Z).

Sharp-Wentworth Technique

$\log \frac{dc/dt}{1-C} = \log(A/ \beta) - Ea/2.303RT(1/T)$

Where β denotes linear heating rate dT/dt, dc/dt= Rate of change of weight fraction with temperature change and c represents the proportion of polymer that has been decomposed at time t. It is possible to create a linear plot of log (dc/dt)/(1-C) *vs* 1/T. The slope of the plot provides the values of Ea and A, which can be deduced using the intercept.

Freeman and Carroll Technique

$\Delta\log(dw/dt)/ \Delta\log w_r = -(Ea/2.303\ R)\ (1/T)/\Delta\log w_r + n$

Where dw = rate of change of weight with time

$w_r = w_c - w$

w_c is the weight loss at the completion of the reaction

w is the total weight loss upto time t

Ea = Energy of activation

A plot of $\Delta\log(dw/dt)/ \Delta\log w_r$ *vs* $(1/T)/\Delta\log w_r$ is a straight line with slope and intercept are (-Ea/R) and n respectively.

In terms of the number of divisions, dw and Wr may be ascertained directly from the thermogram for the purpose of this layout.

Coats and Redfern Technique

$$\int_{T_0}^{T} e^{\frac{-E^*}{RT}}\, dt \simeq (RT^2) \left[1 - 2\frac{RT}{E}\right] e^{\frac{-E^*}{RT}}$$

Plots, log $\frac{[\ln(1-C)]}{T^2}$ *vs* 1/T for (n=1)

$\ln[g(x)/ T^2] = \ln[AR/Be]\ [1-(2RT/E]-(E/RT)$

β = heating rate; A =frequency factor; R= gas constant; T= decomposition temperature; E= activation energy. Plotting g (x) against 1/T gives a straight lines of slope (E/R). Frequency factor is determined from intercept at y-axis[22,23].

FriedmannTechnique

$\ln(d\ \alpha/dt)= \ln(Z) +n \ln(1- \alpha) -(Ea / RT)$

where T is the absolute temperature (K), R is the gas constant (8.314 J/mol), and α represents the conversion at time t. The slope of the linear plot of ln(1- α) *vs* 1/T is used to compute n. The graph is linear and the slope Ea/R used to compute Ea[24].

Results and Discussion

A polymer's viscosity is a proportional indicator of its molecular weight. Using NMP/pyridine as a solvent, a combination of $CaCl_2$ and LiCl was attempted in the Higashi technique and t the polyamide that was synthesized did not have high molecular weight. All the three polymer degrades in conc. H_2SO_4 and so the viscosity of the polymer is expected to be low. PY- PH, PY-CI and PY- SU polyamides which substantially degrade in conc. H_2SO_4 have low viscosities. In fact these three polyamides do not reprecipitate when their solution in conc. H_2SO_4 are poured into water. In the present study, the synthesis of polyamides by the phosphorylation method was therefore slightly modified and carried out with an NMP / Pyridine mixture containing 4% of LiCl, MW assisted IL method and IL method and inherent viscosities are measured for the concentration 0.5 g/dL in conc. H_2SO_4 at 25°C (Table 1). The polymer obtained by microwave assisted ionic liquid method was taken for thermochemical degradation using TGA and DSC studies (Table 2) and corresponding activation energy, free energy,enthapy and entropy was calculated (Table 3).

UV-Visible spectra obtained for polymers are given in Fig. 1(a, b and c). The reason for choosing conc. H_2SO_4 as a solvent for polyamide is its capacity to dissolve the polyamides. In the present investigation n-π transition shows the bands in the visible region and n-π*transition gives bands in the UV region. C=C bonds give absorption signals in UV-Visible spectra only if the compound contains several arrangements of these bonds, where they alternate with single bonds and are in conjugation. Usually non conjugated diene has higher energy and shorter wavelength and are not clearly visible in some cases. Pyrdine C=N ring involving n-n* transition are seen in the visible region at 253nm and 267nm and C=C pyridine ring are seen in 267 nm. C=O amide bonds are seen at 284nm and corresponds to n-n* transition in uv region. The n-π* transition shift to higher wavelength region of 20nm, thus 370nm and 390nm arise due to the delocalization of charge carrier on the ring in PY-PH.

Polyamide's infrared spectra are shown in Fig. 2(a, b and c). Amide band at 3300 $cm^{-1.}$ indicates N-H stretching. The amide I and II bands are thought

Table 1 — Inherent viscosities of polymers

Polymer	Modified phosphorylation method	Microwave assisted IL method	IL method
PY-CI	0.26	0.53	0.41
PY-SU	0.22	0.51	0.38
PY-PH	0.30	0.71	0.59

Table 2 — Thermal properties of polyamides

S. no	Polymer	Temperature (°C) at which % weight loss occur				
		10	20	30	40	50
1	PY–CI	219	277	350	376	404
2	PY–PH	220	355	790	–	–
3	PY–SU	181	197	239	325	733

Table 3 — Activation energy of polymers using different approximation methods

S. No.	Polymer	Coats and Redfern (KJ for n=1 approximation)	Freeman and Carroll (KJ)	Chang (KJ)	Sharp-Wentworth (KJ)	Friedmann (KJ)
1	PY-PH	25.46	22.98	24.03	24.76	24.01
2	PY-SU	15.90	16.41	17.59	16.01	17.48
3	PY–CI	22.98	25.46	26.89	16.73	27.31

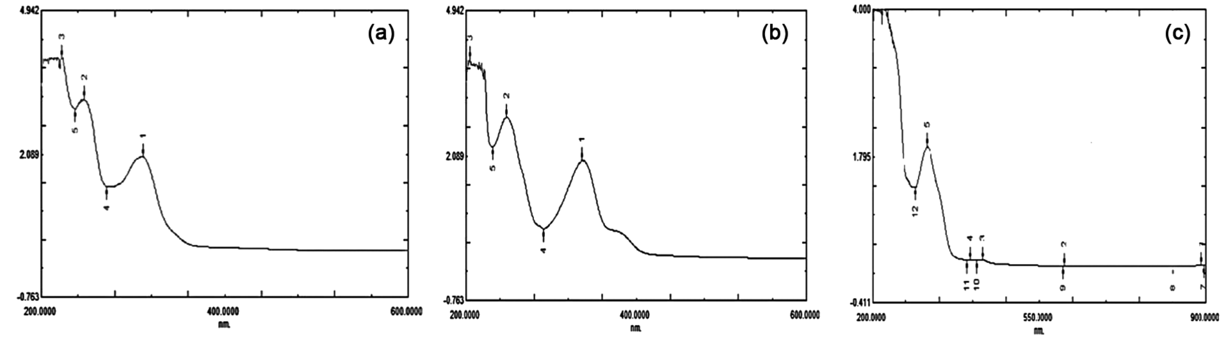

Fig. 1 — UV-Vis spectra of PY –PH, PY –CI and PY –SU

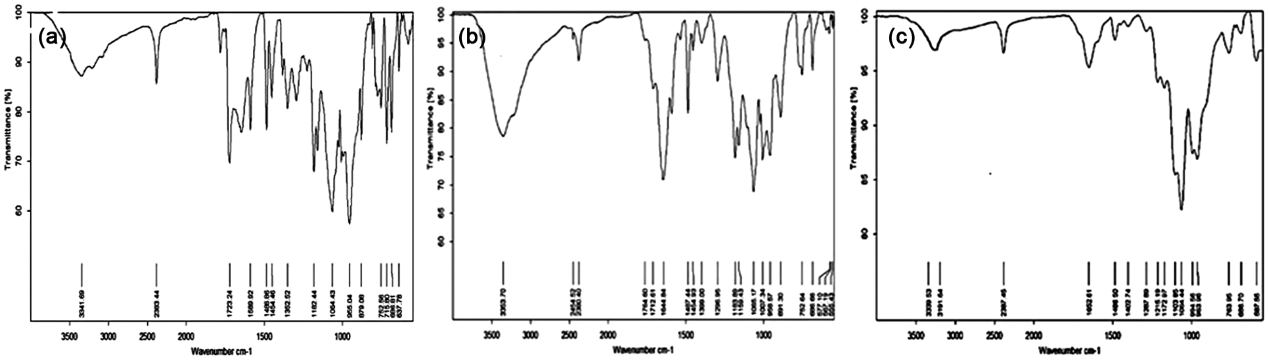

Fig. 2 — IR spectra of PY –PH, PY –CI and PY –SU

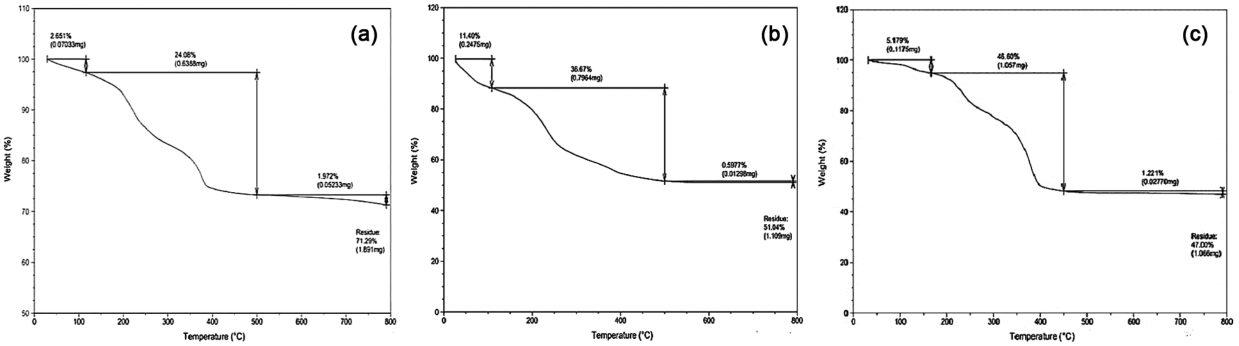

Fig. 3 — TGA curves of PY-PH, PH-CI and PH-SU

to be crucial for polyamide identification, along with the N-H stretching band (in plane-deformation, C-N stretching at 1520 cm^{-1}, and C=O stretching at 1680 cm^{-1}). The combination of C-N stretching and N-H in plane deformations is represented by the amide III band. The amide IV band represents the combination of N-H and C-N stretching. The amide IV band corresponds to N-C=O deformation at 650 cm^{-1} and, N-H out of plane deformation at 700 cm^{-1}is correlated with the amide V band.

The amide VI band is linked to the C-O out of plane at 570 cm^{-1}.The formation of polyamides are further supported by the existence of amide linkage and are confirmed by the presence of representative bands for the amide linkage and the disappearance of characteristics bands caused by the diamine stretching (3300–3500 cm^{-1}), diacids (1680–1715 cm^{-1}), and CH stretching (2500–2700 cm^{-1}). The band at 1680 cm^{-1} confirms the existence of C=O stretch. Since amide comprises N-H and C=O bonds, it is an important group that unites the constituents of amines and ketones. As a result, it displays an incredibly outstanding broad band for the N-H stretch at the left end of the range, which is typically between 3100 and 3500 cm^{-1}.

The band at 1640 cm^{-1} in the pyridine ring corresponds to C=C. The pyridine ring's C=N stretch was identified as the source of the absorption band at 1420 cm^{-1}. At 1110,1100,780, and 730 cm^{-1}, the 2,6 di-substituted pyridine ring produces a characteristic band. The polymers derived from succinic acid gives overtone band 2339, 2360, 2418 cm^{-1}. O=C and-N-H groups are very close to each other to interact internally and forms intramolecular H - bonding. The *trans* orientation of polymers derived from citraconic acid prevents it from performing intramolecular interaction hence >C=O stretching frequency is strong in citraconic acid substituted polymers.

Evaluation of thermogravimetric analysis

Thermogravimetric analysis has been shown to be a useful analytical method for determining the kinetic properties of different materials, providing crucial quantitative information on the materials' strength. TGA/DSC Fig. 3(a, b and c) and DSC Fig. 4(a, b and c) were used to assess the thermal characteristics of PY-PH, PY-CI, and PY-SU in atmosphere of N_2 at 10°C heating rate. Every polymer exhibited nearly identical breakdown characteristics.

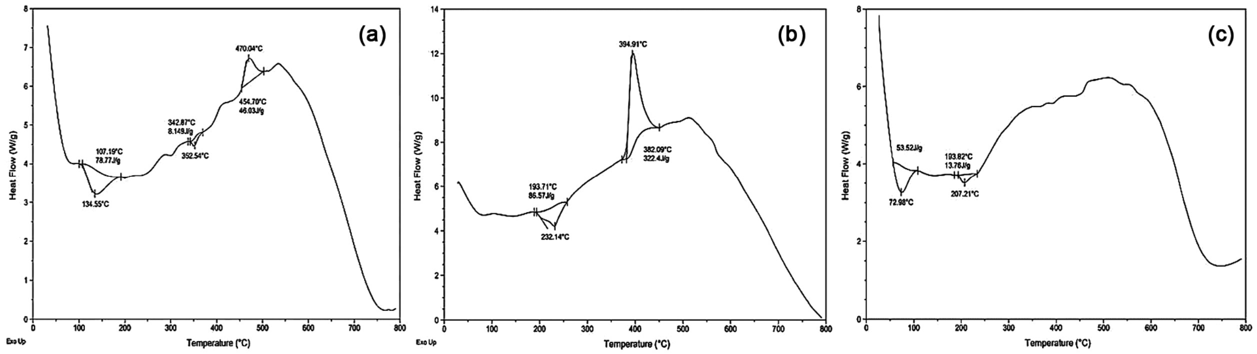

Fig. 4 — DSC curves of PY –PH, PY–CI and PY –SU

PY-PH thermogravimetric measurement shows two stages in breakdown processes. During the first phase one crystalline water molecule trapped within the polyamide is lost. The following stage of the breakdown process begins between 180 and 450°C, which corresponds to a progressive mass loss of 53% calculated and 53% found. The heterocyclic moiety (47% computed and 44.7% found) makes up the residue that remains. DSC diagram also shows two peaks one at 107$^{.c}$ and second one at 470.21^{c} These PAs' char yields in the high-temperature range are quite significant. It says that the heat stability of these polymers is good to moderate.

Thermogravimetric measurements of PY-CI also depicts the two step decomposition processes. The imprisoned water molecule in the polyamide molecule first loses its position. The following stage of the breakdown process begins between 120 and 500°C, which corresponds to a progressive mass loss of 27% calculated and 28.71% found. This results from the citraconic acid moiety's double bond splitting. The heterocyclic moiety (71.29% discovered and 73% calculated) makes up the remaining residue. The DSC diagrams show two peaks corresponding to two stages of degradation, the first peak at 193.1.c and the second one at 394.04°C.

Thermogravimetric measurement of PY-SU shows two stages of the reaction during degradation processes. In the first phase, one crystalline water molecule that is trapped within the polyamide is lost. The following phase of the breakdown process begins around 105–490°C, which corresponds to a progressive mass loss of 44% estimated and 48.96% observed. The aromatic moiety (51.04% discovered and 56% calculated) makes up the remaining residue. The DSC diagram also depicts two peaks corresponding to two stages of thermal decomposition. The first peak makes its appearance at 72.1°C and second one at 192.3°C.

DSC analysis shows the Tg for polyamides which ranges from 140 to 230°C. It demonstrates the moderate to high heat stability of polymers. The twofold melting endotherm (134.5°C and 352.5°C) that PY-PH displays is a typical phenomenon seen in semi-crystalline polymers. (134.5°C and 352.54.) 134.55.c is the crystalline temperature while474.4°C is the melting temperature. The DSC curve also revealed that PY-SU polyamides melt at a lower temperature than aromatic polyamides and had a lower glass transition temperature lower than PY-PH polyamides. Hence, when the polymer chain stiffens, the melting temperature rises. Because of the stiffness effects coupled with conjugation, aromatic polyamides melt at a greater temperature than their unsaturated and saturated aliphatic polyamides.

From the thermal decomposition pattern, it is evident that the primary polyamide chain scission occurs either at the amide bond or at the adjacent bond. Homolytic scission and intramolecular C-H transfer are suggested as the possible primary chain scission processes. Pyridine rings are stabilized in the process of pyrolysis of PY-CI. The cleavage of the C-N amide bonds in PY-PH are the primary pyrolysis pathway. The high char yield of 72% proved that alkenes are easy to take part in homolytic radical scission at C=C of PY-CI polyamide[25].

According to the Van Krevelen and Hoftzer equation, char yield may be used as a criterion for assessment (LOI) of the polyamide.

LOI= 17.5 +0.4 CR CR–charyield. PY -PH: 33.90 PY -CI: 46.02 PY-SU:37.92

Based on their char production, the polyamides PY-SU and PY-CI have LOI values greater than 37.

Polymers can be classified as self-extinguishing based on their LOI value.PY-CI, per the above equation, is a self-extinguishing polymer. The DTG curve also shows that the sample's pyrolysis caused a transition that centered around 180°C. The activation energies obtained from Chang and Sharp-Wentworth are in good agreement with each other. Nevertheless, Freemann and Carroll's approach differed slightly. This might be because of the tangent dw/dt, which causes distinct differential functions over a brief period of time.

By employing the least square method all linear plots were drawn and the corresponding correlation coefficient calculated. Regression analysis was also carried out for all the three polyamides and the best fit method was determined for each and every stages of decomposition. It is clear from the data's obtained for energy of activation, the polyamide PY-CI showed highest energy of activation. The first stage of decomposition followed Janders model (Ea=70.68 KJ/Mol & R2=68.32). and the second stage of decomposition followed second order kinetics model (Ea=26.63 KJ/mol and R2=96.70). The first stage of decomposition for PY_SU followed Janders model(Ea=48.88 KJ/mol and R2=65.86). and the second stage of decomposition followed second order kinetics model (Ea= 9.31 KJ/mol mol R2=89.39). The first and second stage of decomposition for PY-PH followed Janders model(Ea=51.07 KJ/mol and R2=83.97). and second stage of decomposition followed Cranks model. (Ea= 44.80 KJ/mol and R2=97.79). Thus it is evident from the regression analysis that for all the three polyamides the first stage of decomposition followed Janders model of kinetics and second stage of decomposition corresponds to second order kinetics model except for PY_PH which follows Cranks model.

Theoretical Consideration

Free energy change (ΔG)

Using Coats -Redfern approach when the activation energy was determined the least inaccuracy is obtained (Table 4),

$\Delta G = \Delta H - T\Delta S$,

ΔH-Enthalpy change; ΔS - Activation energy; T = Temperature (K) and ΔS = Entropy change. From the graph, A was found from the intercept and E from the slope.

Calculation of change in entropy

Intercept = log (KR/ hE)+ΔS/2.303R

$K=1.3806\times10^{-16}$erg/deg/mole

$\Delta S = R[\ln(Ah/KT)]$

$\Delta H=E-RT$

R=1.987cal/deg/mol (or) 8.314 J/K/Mol

ΔS=change in entropy

h=Planck's constant 6.625×10^{-27}erg/sec E = Activation energy

Free energy change can be calculated using $\Delta G = \Delta H - T\Delta S$

The level of thermal activation energy is undoubtedly difficult to interpret because the degradation component is meant to be complex. Activation energy levels are positive because of the polymer's oxidation-reduction processes. All the techniques provide graphs that are genuinely straight lines. From the graph it is clear that the polymer degradation does not fully obey first order kinetics (Table 5, Fig. 5a–e). Therefore, in order to obtain a clear image of the majority of the points for the

Table 4 — Energy of activation with various kinetic models for the polyamides showing R^2 value by Coats and Redfern method

			PY-CI		PY-PH		PY-SU	
S. N0	MODEL	$g(x)$	I Stage	II Stage	I Stage	II Stage	I Stage	II Stage
1	First order	$\ln(1-\alpha)$	22.68 (R^2 =80.33)	24.88 (R^2 =92.91)	32.67 (R^2 =64.89)	14.51 (R^2 =96.17)	22.00 (R^2 =60.64)	4.50 (R^2 =66.10)
2	One dimensional diffusion	$(\alpha)^2$	18.78 (R^2 =83.64)	36.42 (R^2 =97.54)	69.99 (R^2 =67.89)	22.24 (R^2 =89.81)	47.52 (R^2 =64.77)	10.60 (R^2 =78.23)
3	Crank	$(1-2/3)\alpha(1-\alpha)^{2/3}$	50.909 (R^2 =83.85)	44.80 (R^2 =97.79)	70.45(R^2 =68.18)	28.20 (R^2 =94.92)	48.42 (R^2 =65.49)	13.65 (R^2 =88.12)
4	Janders	$[1-(1-\alpha)^{1/3}]^2$	51.07 (R^2 =83.97)	44.97 (R^2 =96.92)	70.68 (R^2 =68.32)	31.99 (R^2 =96.69)	48.88 R^2 =65.86)	15.39 (R^2 =87.80)
5	Second Order	$(1-\alpha)^{-1}$ -1	23.06 (R^2 =80.95)	43.38(R^2 =81.89)	33.20 (R^2 =65.42)	26.63 (R^2 =96.70)	23.03 (R2 =62.80)	9.31 (R^2 =89.39)
6	Contracting Cylinder	$1-(1-\alpha)^1$	22.48 (R^2 =80.0)	18.21 (R^2 =96.42)	32.43 (R^2 =64.33)	10.02 (R^2 =89.21)	21.45 R^2 =59.64)	2.48 (R^2 =37.57)
7	Contracting Spherical	$1-(1-\alpha)^{1/3}$	22.56 (R^2 =80.12)	20.33 (R^2 =95.69)	32.50 (R^2 =64.45)	11.40 (R^2 =92.49)	21.62 R^2 =59.98)	2.88 (R^2 =48.85)

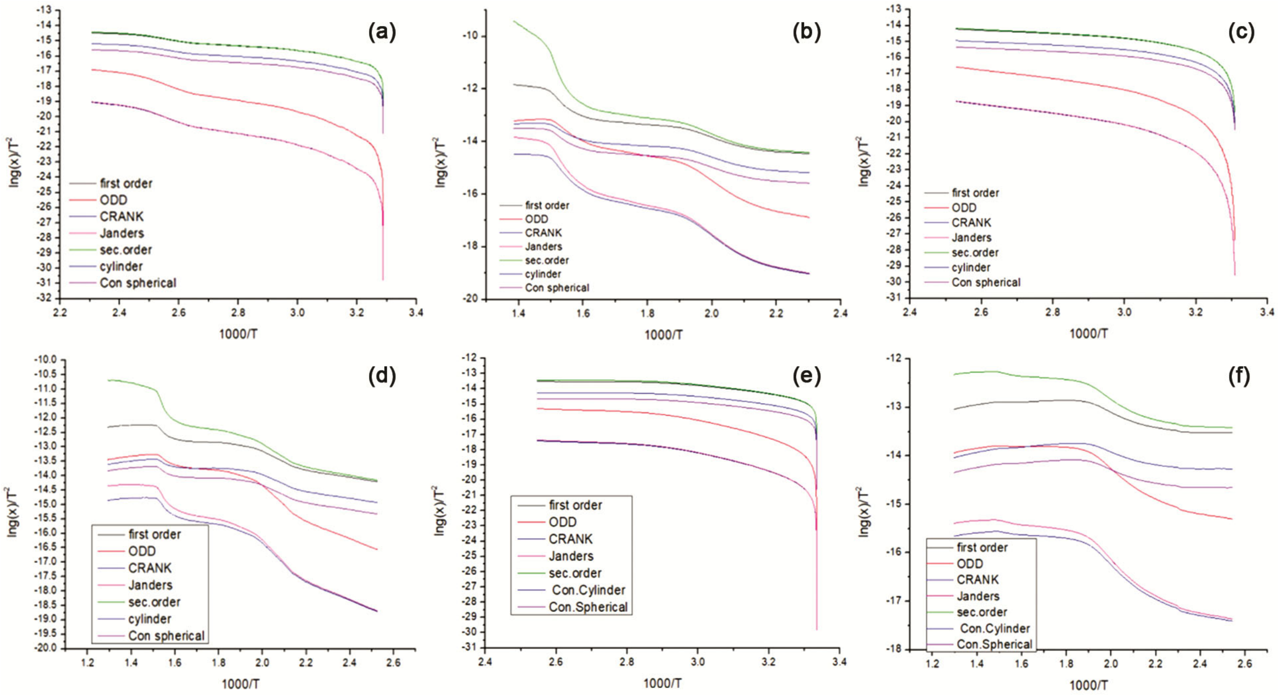

Fig. 5 — Kinetic model for PY –PH, PY –CI and PY –SU stage 1 and stage 2

Table 5 — Kinetic parameters for the thermal decomposition of polyamides

Polyamide	E (KJ mol^{-1})	ΔH (KJ)	ΔS (J)	ΔG (KJ)
PY-CI	22.98	22.12	–2.647	1095.26
PY-SU	15.90	15.01	–3.372	1522.29
PY-PH	25.46	24.82	–4.421	1444.92

Freeman and Carroll technique, certain irregular points were missed. The three polyamides' ΔG values are all positive, indicating that the dissociation process is not spontaneous. For each of the three polyamides, the positive value of ΔH shows that the compound is flexible and has several degrees of freedom for vibration and rotation. The breakdown temperature of PY-SU was lower than that of PY-PH among the three synthesised polyamides. Therefore, when comparing PY-SU to the other two polyamides, it can be said that it has high thermal stability.

Since the backbone of many polymers is a carbon-carbon chain, the stability of the C-C bond determines how stable the polymer will remain thermally. Taking PY-SU and PY-PH as examples, we can see that the stability of the polymer backbone bond reduces as we move from left to right in terms of substituent count. As a consequence, PY-PH is less stable thermally than PY-SU.

Conclusion

The phosphorylation technique of producing polyamides was somewhat altered in the current work. The intrinsic viscosities in concentrated H_2SO_4 at 25°C were measured for all the polyamides using all the three methods of synthesis at 0.5 g/dl. It was discovered that PY-PH made using the microwave aided IL process had greater viscosity. The produced polyamides underwent extensive characterization, and thermal characteristics were investigated. The Van Krevelen and Hoftzer equation states that PY-CI is a self-extinguishing polymer. The DTG curve also demonstrates that the sample's breakdown caused the transition to centre at around 180°C.Activation energies were calculated for all the three polyamides using Coats & Redfern, Chang, Sharp Wentworth, Freemann-Carroll and Friedmann technique. The polyamide PY-PH showed higher activation energy when compared to other counterparts. The regression analysis employing Coats -Redfern method was carried out using various kinetic models for all the three polyamides for all the stages of decomposition. Best linear fit model was taken. It was found that stage I of all the three polyamides decomposition processes followed Janders kinetic model and the second stage of decomposition followed mostly second order kinetics. Taking the approximation of

Coats -Redfernn method for (n=1), kinetic parameters were calculated. Positive values of activation energy of the polyamides indicate polymer's oxidation-reduction processes. For each of the three polyamides, the Δ G and ΔH values were positive. Consequently, it suggests that the dissociation process is non spontaneous in nature. It is clear from the literature that the stability of the C-C bond affects thermal stability. Incorporation of aromatic units in the polymer main chain increases the thermal stability because they have no degrees of freedom to rotate and and partly due to aromatic pi-pi interactions the polymer back-bone are held in their place. As a result, PY-PH is thermally stable and PY-SU is not.

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