

Study on the Thermal Decomposition Kinetics and Calculation of Activation Energy of Degradation of Poly(*o*-toluidine) Using Thermogravimetric Analysis

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ABSTRACT: Thermo Gravimetric Analysis (TGA) analysis was employed to investigate activation energy (E_a) for the process of degrading of poly(*o*-toluidine) (POT) applying Horwitz & Metzger, Coats & Redfern and Chan et al., methods. POT was synthesized by chemical oxidative polymerization method using Ammonium per Sulphate (APS) as an oxidant while Dodecylbenzene Sulphonic Acid (DBSA) and sulfuric acid as co-dopants. Different samples, synthesized by variations in the reactions parameters, were evaluated in order to choose the one with the highest activation energy of degradation. Additional characterization of the polymer was carried out through different techniques such as Scanning Electron Microscopy (SEM), UltraViolet Visible spectroscopy (UV-Vis) and X-Ray Diffraction (XRD) analysis.

KEYWORDS: POT; TGA; XRD; SEM.

INTRODUCTION

The practical applicability of Intrinsically Conducting Polymers (ICPs) depends on their electrochemical properties,

environmental and thermal stabilities [1]. Although their methods of preparation, morphology and electrochemical

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characterizations have been extensively studied, research on the evaluation of the thermal properties has received less attention. Only a small amount of work has been devoted to this subject [2]. Thermal stability of ICPs is useful for their applicability to technologies [3]. Thermo Gravimetric Analysis (TGA) is the main and important technique for measuring the weight loss and its rate of change with respect to temperature/time in a controlled atmosphere. TGA studies are generally used for finding the material composition and its thermal stability up to very high temperatures. In this study, weight loss stages are investigated for the amount/percent (%) weight loss, the amount/percent (%) of the non-combusted residue with a change in temperature as well as the temperature of different degradation steps.

The data obtained from TGA is applicable for calculating kinetic parameters of degradation of the polymer. Moreover, an integral analysis method is used for performing kinetic study of mass loss vs. temperature (i.e. integral curve), obtainable from TGA directly. One of the limitations of this method is that the temperature integral is not a precise method for linear heating rate program. Several researchers have developed different methodologies, among them *Horowitz-Metzger*, *Coats-Redfern*, and *Chan et al.* methods are well-liked methods [2].

Polyaniline is one of the most attractive conducting polymers [4-6]. However, its practical utilization has been restricted by its insolubility in organic solvents because of the delocalized π - bonds along their backbone [7]. Methyl-substituted derivative of polyaniline (PANI), called Poly(*o*-toluidine) (POT), [8, 7] shows properties very similar to PANI, with improved solubility [9, 10] and processability [11]. *o*-Toluidine is used for its polymerization, which is a low cost and its conversion into the polymer is a simple process [12]. In this article, optically active POT salt was prepared and comprehensive study about the thermal degradation of the obtained polymer was carried out by using three methods proposed by *Horowitz Metzger*, *Coats-Redfern* and *Chan et al.*, To the best of author's knowledge no detailed study is available to find out activation energy for POT in its salt form.

EXPERIMENTAL SECTION

Materials

Throughout the experimental work research grade reagents were used. *O*-toluidine, OT, (Acros) was distilled

before use. Dodecylbenzenesulfonic acid (DBSA) and acetone were purchased from Acros, while chloroform, sulfuric acid (H_2SO_4) and ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ from Riede-de haen and were used as it is.

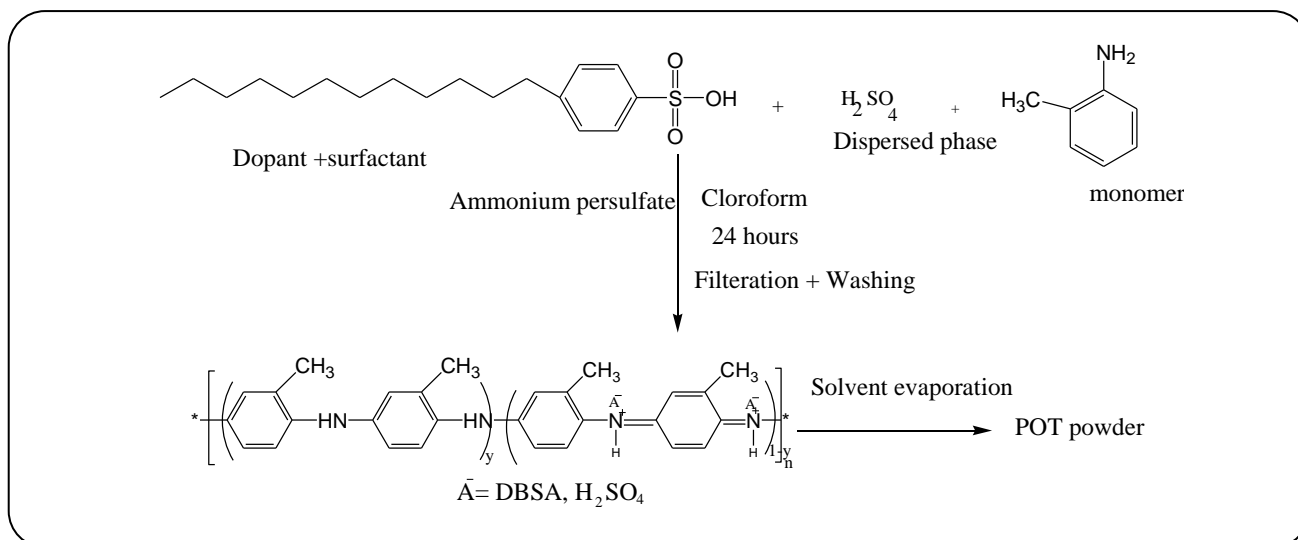
Synthesis

POT salt was prepared by using the previously reported method [13]. In the typical experiment, chloroform (50 mL) was transferred to a round bottom flask. Afterward, 2.3 ml of DBSA was mixed in it under constant mechanical stirring. Following this, 1.5 mL of OT and 25 mL of 0.5 M H_2SO_4 were added to the above solutions. 25 mL of 0.05 M ammonium persulfate was added to the resulting mixture which slowly turned green. This polymerization process was performed for 24 h. Finally, the organic phase having POT was isolated and washed with 50mL of acetone thoroughly. Afterward, a dark green highly concentrated POT salt was separated (Scheme 1), which was dried in a Petri dish. Then a small amount of acetone was added to the petri dish which broke the films into flakes. Lastly, pure POT salt was collected by filtration which was dried in a desiccator.

The experimental conditions were optimized by varying the concentration of H_2SO_4 . The POT prepared with varying concentrations of H_2SO_4 were named POT-1, POT-2, POT-3, POT-4 and POT-5 where H_2SO_4 concentrations were 0.3M, 0.5M, 0.9M, 1.3M, and 1.7M, respectively.

Characterizations

Cyclic Voltammetry (CV) of POT salts was carried out in a three electrode electrochemical cell using 3000 ZRA potentiostat/galvanostat Gamry (USA). POT salt was dissolved in chloroform and dip coated on gold sheet electrode, used as a working electrode. Whereas, a coiled wire of gold and Saturated Calomel Electrode (SCE) were used as counter electrode and as a reference electrode, respectively. 2 M H_2SO_4 was used as an Electrolyte. Ultraviolet-Visible (UV-Vis) spectrum was obtained using Perkin Elmer (UK) Spectrophotometer. A quartz cell of 1cm path length was used for recording spectrum of PANI-DBSA dissolved in chloroform. X-ray diffraction (XRD) pattern was recorded using $\text{Cu K}\alpha$ radiations ($\lambda = 1.5405 \text{ \AA}$) on a Rigaku (Japan) X-ray diffractometer. Thermal analysis of the polymer was carried out by using



Scheme 1: Synthesis of POT.

Perkin Elmer (USA) at a heating rate of $10^\circ/\text{min}$ in the presence of an N_2 atmosphere. Size and Morphology of the particles were evaluated with a scanning electron microscope [JSM-5910, JEOL].

RESULTS AND DISCUSSION

Cyclic Voltammetry

Cyclic Voltammograms (CVs) of POT salt at 30 mV/s scan rate are shown in Fig. 1. CV display two couples of redox peaks [14]. The first anodic peak at $E_{\text{SCE}} = 0.299\text{-}0.35\text{ V}$ is due to the conversion of leucoemeraldine form of POT towards emeraldine form. The second peak at $E_{\text{SCE}} = 0.52\text{-}0.56\text{ V}$ is assigned to the transformation of the emeraldine form of PANI to pernigraniline [15] as shown in Scheme 2 [7]. The radical cations that were generated at $E_{\text{SCE}} = 0.299\text{-}0.35\text{ V}$ persist in the POT films till the potential reaches to $E_{\text{SCE}} = 0.52\text{-}0.56\text{ V}$ where fully the oxidized pernigraniline is formed. Two cathodic peaks observed in the reverse sweep demonstrate the reduction process [16]. The intermediate peak between first and second oxidation peak is absent in the CV of all samples, indicating the absence of any degradation products [17]. From Fig. 1, for POT 5 there is a positive shift in the first redox peak potential. This positive shift can be explained by the higher relative intensity of quinoid to benzenoid ring modes of POT. The quinoid units are more electron withdrawing than benzenoid unit and thus shift the first anodic peak to higher potential [17].

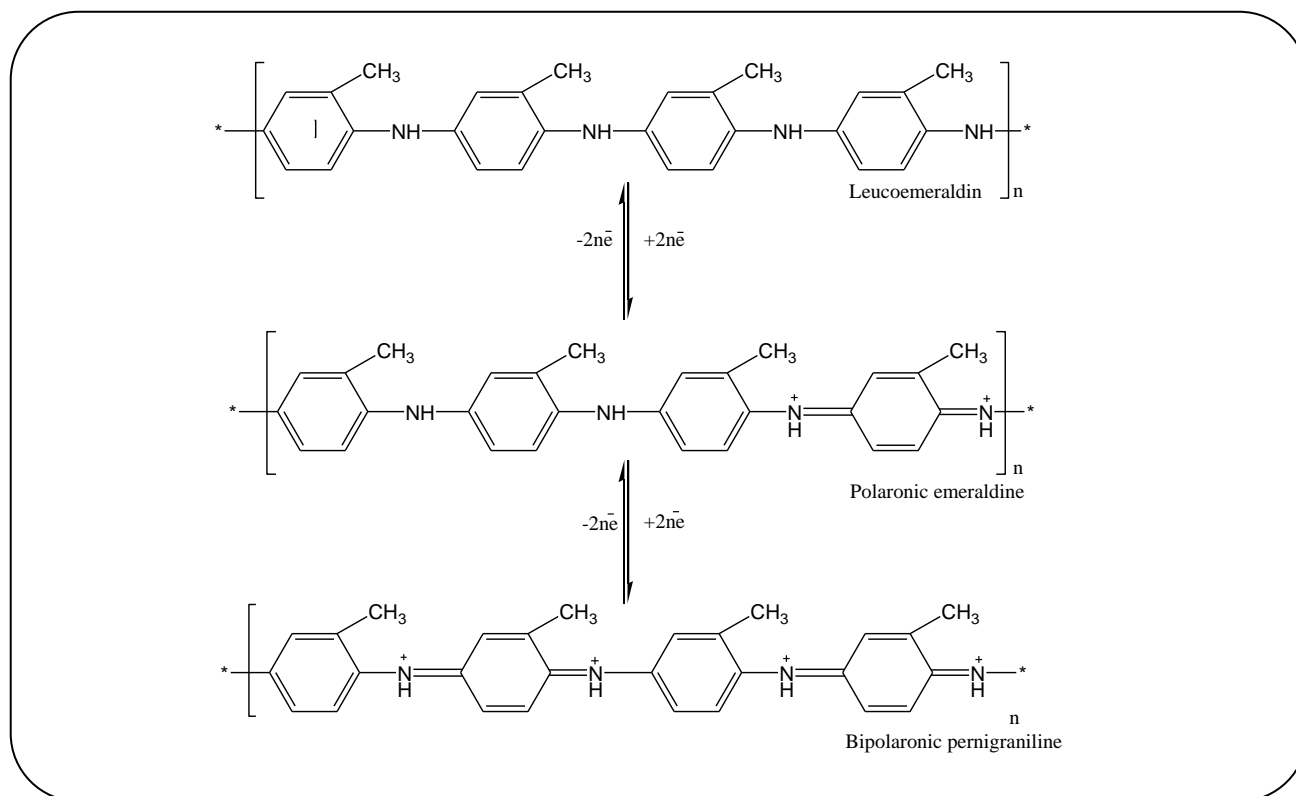
Thermo Gravimetric Analysis

Thermo Gravimetric Analysis (TGA) is a suitable and very useful technique for determination of dopants level and water content in the polymers. Beside this, it is useful to determine the thermal degradation pattern, structural aspects, and thermal stability [18]. The degraded matter at each step of the curve can be determined through the mass loss profile.

The TGA results of the POT salts prepared with various H_2SO_4 concentrations are given by their thermograms and are presented in Fig. 2. POT salts prepared at room temperature presents weight loss in three steps [19]. The first step is due to the moisture loss. The second step (i.e. 48 - 66%), is due to destruction of $\text{NH}^+\text{.....SO}_3^-$ interactions, which exists between the POT chain & dopant (i.e. DBSA). The third step is noted to be somewhat slow and gradual which is because of the chain degradation of POT backbone. As presented in the Fig. 2, all POT salts were not destroyed completely because of carbonization of the synthesized POT salt in a nitrogen atmosphere which leaves some residue. Moreover, POT salts prepared in this work showed the highest thermal stability reported, so far.

Kinetic Analysis of TGA Data:

Significant kinetic parameters (pre-exponential factor, activation energy, order and mechanism of a reaction) can be calculated by using TGA. Knowledge of these parameters is important for investigating thermal stability and hence



Scheme 2: Reaction scheme for the electrochemical process of POT film in the acidic electrolyte solution.

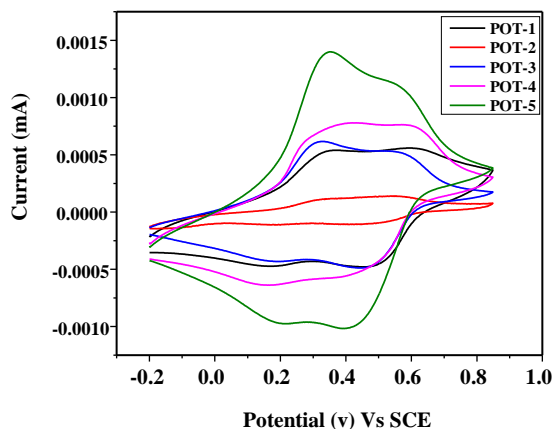


Fig. 1: CVs of POT salts, as indicated.

the behavior of the materials in high temperatures [3]. Various methods have been developed for the determination of kinetic parameters of solid-state reactions. Generally, the kinetics of the condensed and heterogeneous phase reactions in the non-isothermal state is given by the following an expression.

$$\beta \left(\frac{d\alpha}{dT} \right) = A f(\alpha) \exp(-E_a/RT) \quad (1)$$

In Eq.(1), $f(\alpha)$ is a differential conversion function, α is the degree of transformation, T is the temperature, β is the linear heating rate, A is a pre-exponential factor, E_a is activation energy, R is gas constant [20].

The kinetic triplet (A , E , $f(\alpha)$) can be determined differential, integral or other. In present work, three well-liked methods applied for evaluating kinetic parameters for the degradation of synthesized POT salts which assumes first order kinetics.

a) Horowitz and Metzger method

Horowitz and Metzger derived an equation for extraction of pyrolysis parameter by using TGA. According to this method, a plot of $\ln[\ln \{(W_o - W_f) / (W_t - W_f)\}]$ $\ln[\ln \{(W_o - W_f) / (W_t - W_f)\}]$ (double logarithm of the reciprocal of the reactant weight) versus temperature gives the activation energy of degradation. For the first-order reaction, they developed the following equation [21, 22].

$$\ln[\ln \{(W_o - W_f) / (W_t - W_f)\}] = E_a \theta / RTs^2 \quad (2)$$

Whereas

W_o is weight at the start of the experiment, W_t is the weight of the material at onward temperature, W_f is weight at the end,

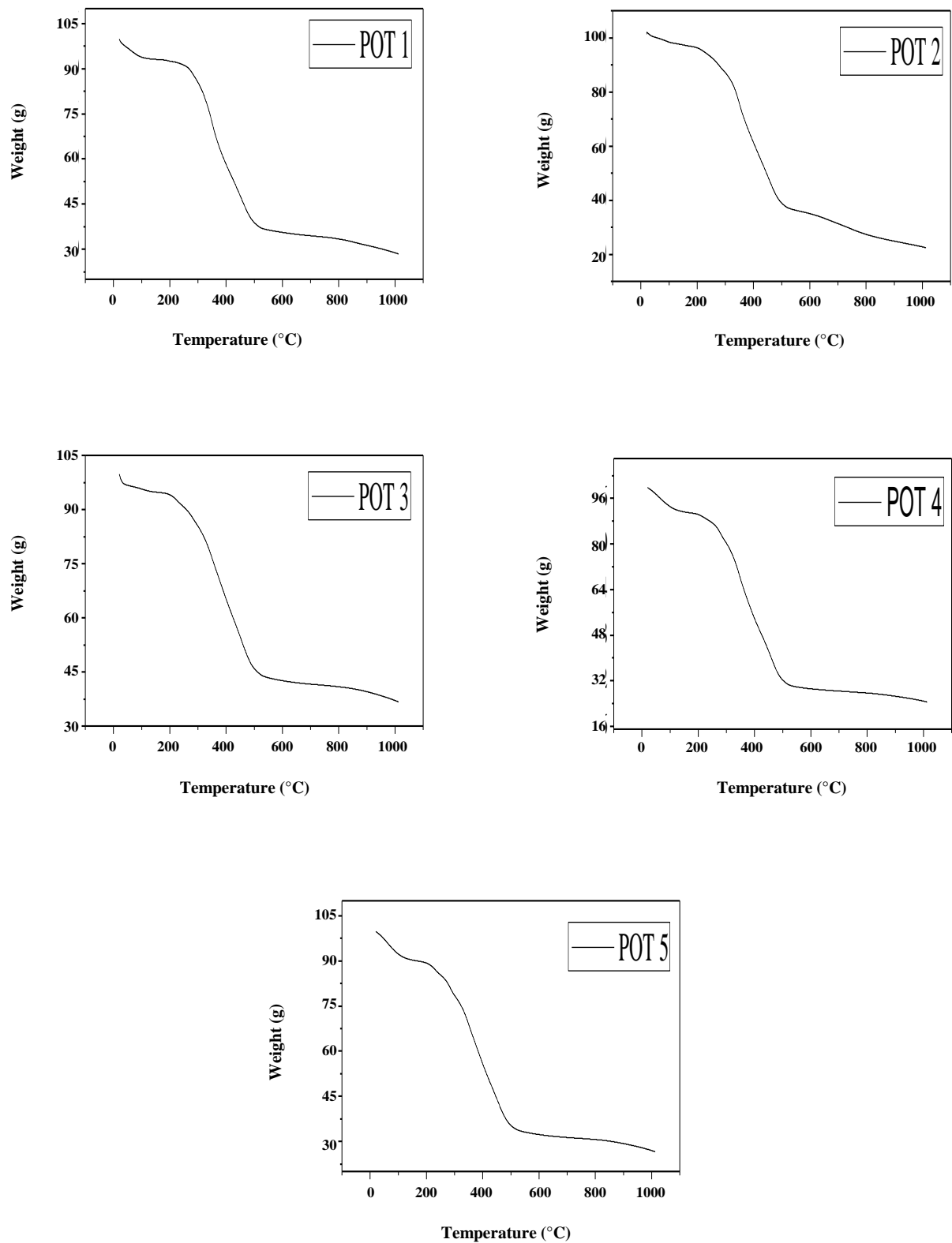


Fig. 2: Thermogravimetric curves for POT salts.

R is general gas constant and θ is equal to $T-T_s$ where T_s is the reference temperature which can be obtained from the following relation:

$$(W_t - W_f) / (W_o - W_f) = 1 / e$$

Thus activation energy can be calculated from the slope ($E_a \times 10^3 / RT_s^2$) of a plot of the double logarithm of the reciprocal of the weight fraction of the reactant versus temperature.

b) Coats and Redfern Method

Coats and *Redfern* introduced a relation for determination of activation energy (E_a) where the order of reaction is important. The equation is as given below [23].

$$\log [1 - (1-\alpha)^{1-n} / T^2 (1-n)] = \log [(AR/\alpha E_a) \{ 1 - (2RT/E_a) \}] - (E_a / 2.303 RT) \quad (3)$$

When n is 1 i.e. first order reaction, $\text{Log} [-\log(1-\alpha) / T^2]$ against $1000/T$ gives a plot of a straight line with a slope ($E_a/2.303R$) for determination of E_a .

c) Chan et al. Method

Chan et al. used the Arrhenius plot for the calculation of activation energy by assuming first-order reaction kinetics [25]. Arrhenius plot of $(\ln k/w)$ vs $1/T$ gives the slope ($-E_a/R$). The slope of this plot gives activation energy of degradation of the material whereas k is the rate of percent weight loss; w is the corresponding percent weight of the remaining material.

Thermograms of POT salts are given in Fig. 2 and Fig. 3-7 show graphs using TGA data. The activation energies were calculated by using *Horowitz and Metzger*, *Coats and Redfern*, and *Chan et al. Method* are 27.06-38.10 kJ/mol, 20.47-25.84 kJ/mol, and 21.30-28.84 kJ/mol, respectively.

The results show that when experimental data of TGA was analyzed by different methods of analysis, the calculated values for kinetic parameters were not similar. This phenomenon was explained by *Brown* [25]. Detail study was carried out regarding the calculation of E_a using non-isothermal data. The authors proposed that a variation in the values are because of the way in which the integral method has been derived. These equations have been developed by assuming that activation parameters are independent on α (degree of conversion).

In this study, the magnitude of activation energy changes sequentially by using the three methods (Table 1). It has been observed that the activation energies calculating

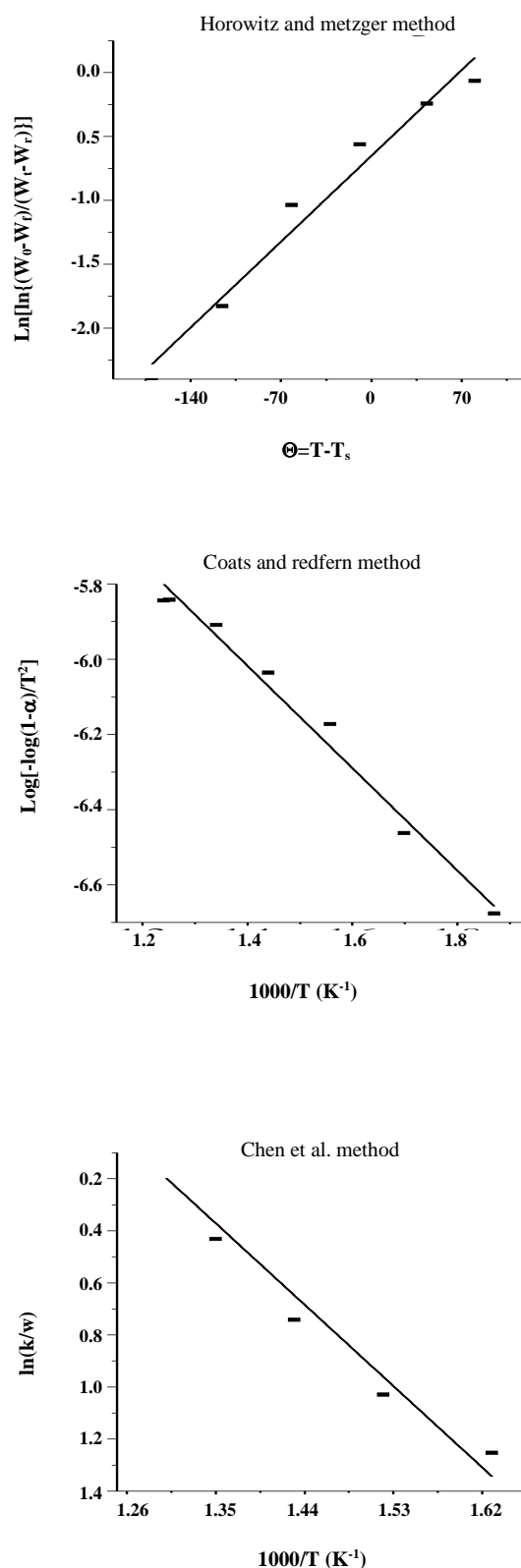


Fig. 3: Plots for obtaining activation energy of POT-I.

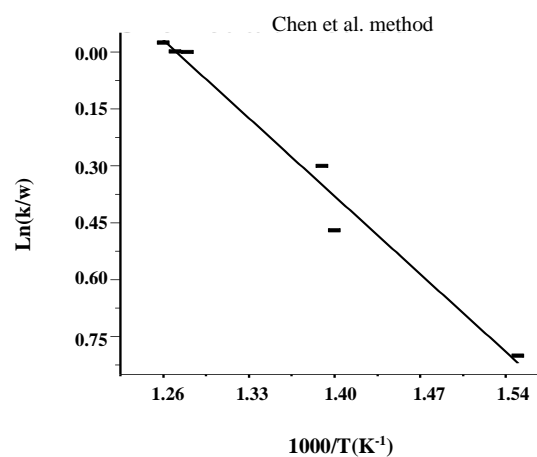
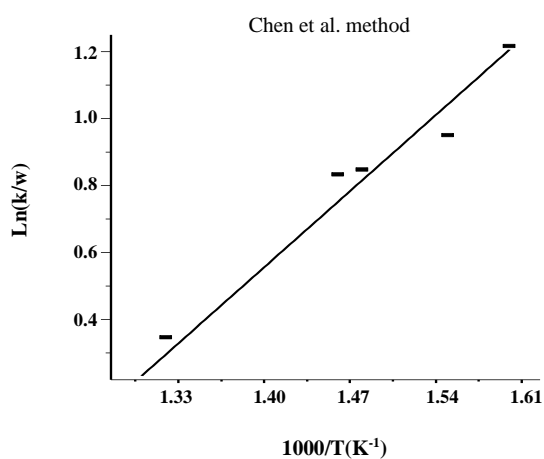
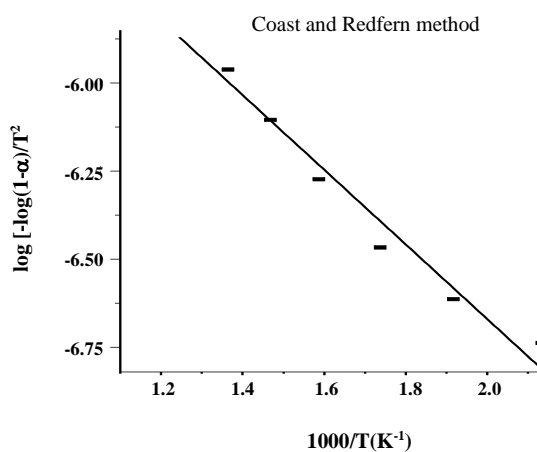
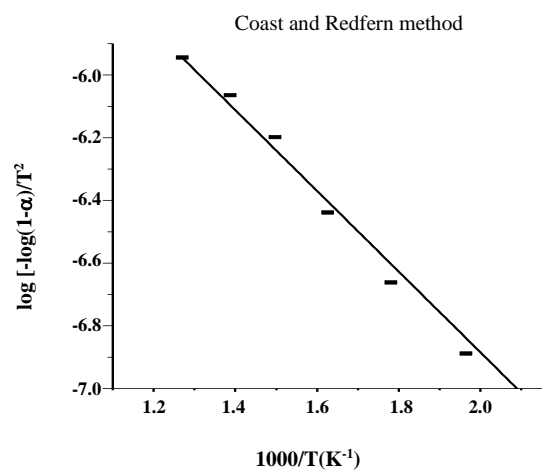
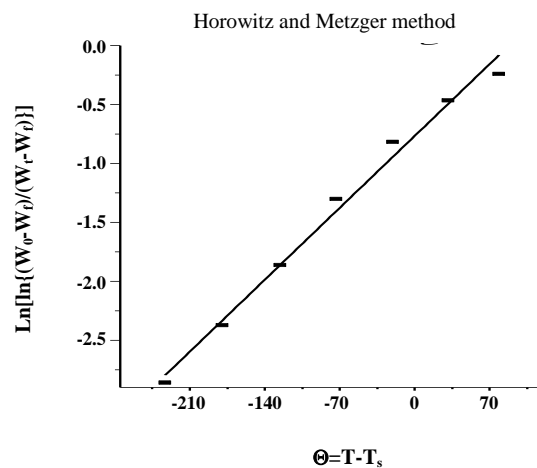
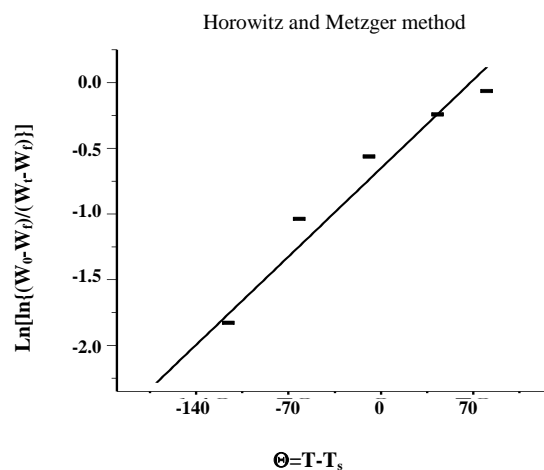


Fig. 4: Plots for obtaining activation energy of POT-2.

Fig. 5: Plots for obtaining activation energy of POT-3.

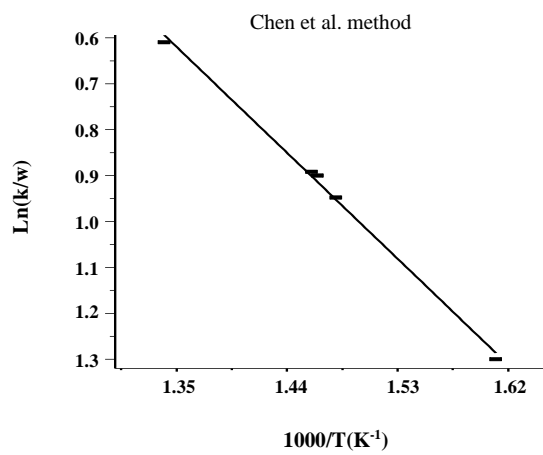
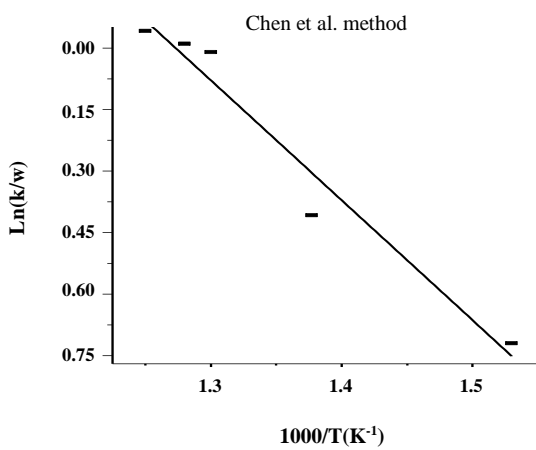
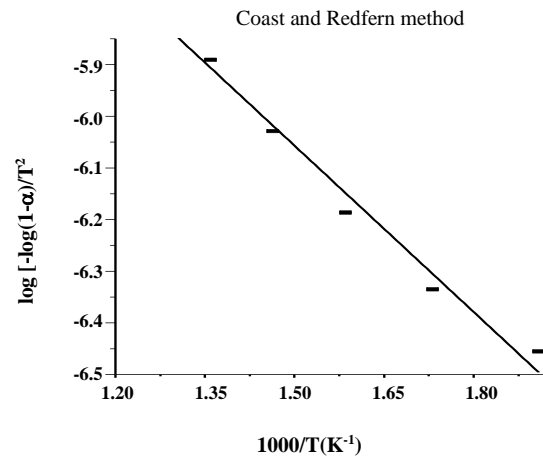
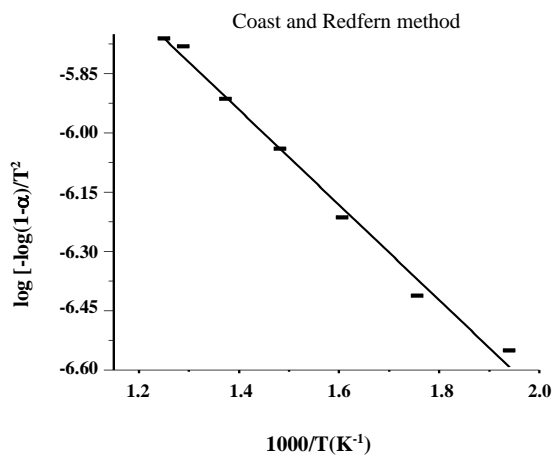
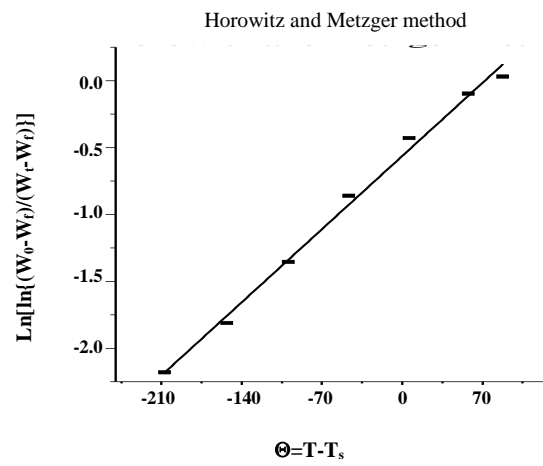
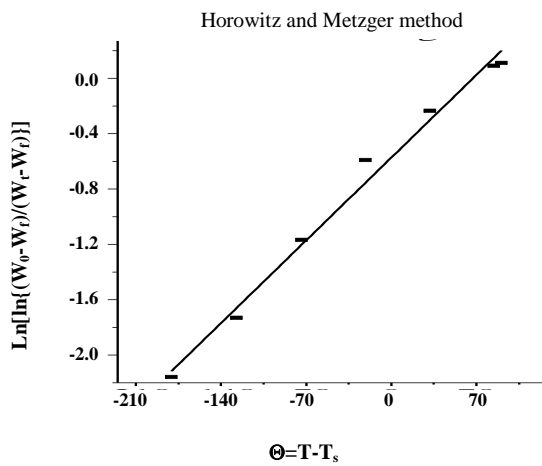


Fig. 6: Plots for obtaining activation energy of POT-4.

Fig. 7: Plots for obtaining activation energy of POT-5.

Table 1: Activation energy for POT salts.

Sample	Activation Energy (kJ/mol)		
	Horowitz and Metzger Method	Coats and Redfern Method	Chan et al. Method
POT 1	38.10	25.84	28.84
PO1 2	38.46	24.60	26.93
POT 3	32.59	20.28	24.36
POT 4	30.75	22.96	24.27
POT 5	27.06	20.47	21.30

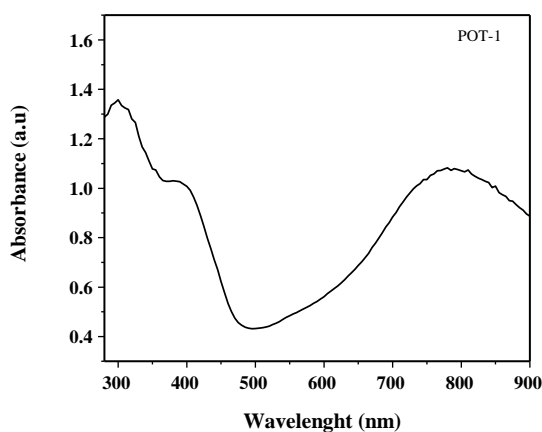


Fig. 8: UV-Visible spectrum of POT-1.

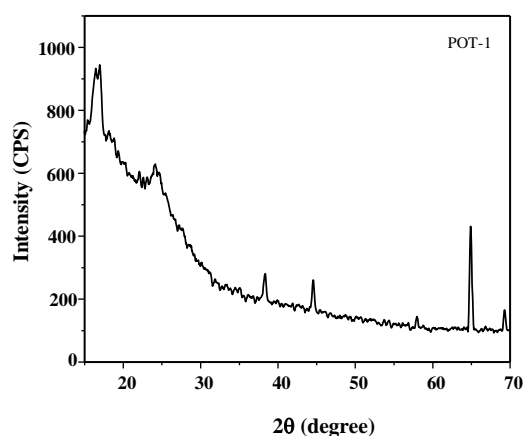


Fig. 9: XRD pattern of POT-1.

by using Coats and Redfern method are less than the calculated values by the other two methods. Whereas, the E_a values calculated by the method of *Chan et al.*, are less than the E_a values acquired by *Horowitz and Metzger* method and greater than Coats and Redfern method. These variations among the activation energies calculated by using the three methods can be due to different approximations of the temperature integral [3]. These values may not be the most accurate, but give an approximate range of the parameters. The data of activation energy calculated by each specific method can be obtained conveniently for comparison of the relative thermal stabilities of the different polymers.

UV-Visible Spectroscopy

The UV-Visible spectrum of POT-1 was recorded in chloroform (Fig. 8). The peak observed at 300 nm is due to $\pi-\pi^*$ transition of benzenoid rings [15]. The characteristic absorbance peak at 395 nm in the spectra of POT corresponds to polaron transition arising due to quinoid ring [26]. The doped polymer has shown the extended

band at 789 nm due to the bipolaron transition. This peak confirmed the conductive emeraldine salt form of POT [27].

X-ray Diffraction (XRD) Analysis

XRD patterns are useful for investigating the nature, composition, and structure of ICPs. Crystallinity and orientation of conducting polymers are of much interest, due to their highly ordered system which reflects the conductive state [28].

In Fig. 9, the XRD pattern shows that POT salts are semicrystalline materials. The Figure presents some intense and sharp peaks of POT salts. The sharp and intense peaks are located at $2\theta \approx 14^\circ, 16^\circ, 38^\circ, 44^\circ, 64^\circ$ and other peaks at $2\theta \approx 24^\circ, 38^\circ, 57^\circ, 69^\circ$. The peak at $2\theta \approx 24^\circ$ is due to the reflecting/scattering of radiations perpendicular to the chain. This presents high crystallinity of the material which may be due to substitution and hydrogen bonding between hydrogen of one ring and a sulfonic group of the other ring of the adjacent chain [29].

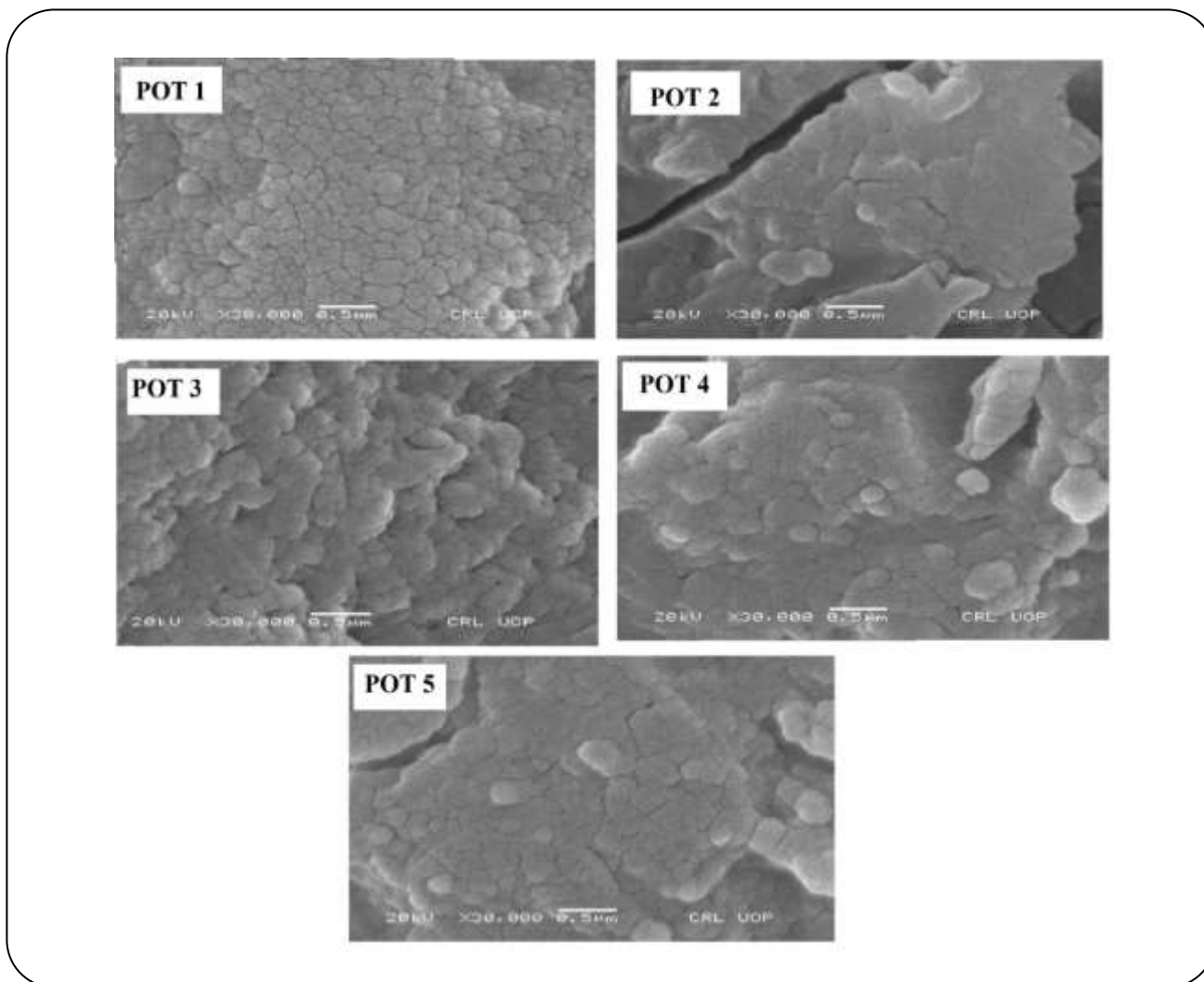


Fig. 10: Scanning Electron Micrographs of POT salts.

Scanning Electron Microscopy (SEM)

Generally, it has been found that nature of oxidant, dopant and synthesis method greatly affect the morphology of polyaniline and its derivatives. SEM micrographs of the synthesized POT salts are shown in Fig. 10 which shows flakes of POT have a smoother surface and little pores. The flakes may be produced due to some random three-dimension growth of the polymer [30]. Moreover, irregular structures were obtained in these images with little alterations in the morphology which demonstrates that the amount of H_2SO_4 does not affect the morphology of POT salts significantly. Conversely, the porosity decreases as the concentration of H_2SO_4 increases (i.e. from POT-1 to POT-5). This may be due to the enhanced doping level [31].

CONCLUSIONS

A detailed kinetic study of POT salts was carried out based on the thermogravimetric analysis. Activation energy calculated by using Horwitz & Metzger, Coats & Redfern and Chan et al., methods were 27.06-38.10 kJ/mol, 20.47-25.84 kJ/mol, and 21.30-28.84 kJ/mol, respectively. The difference in the values of activation energy of degradation calculated via different methods can be ascribed to the difference in the parameters of the equations. However, all the values suggest sample POT-1 to be the most stable amongst all POT samples in the present work.

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