

Kinetic studies of polystyrene using non - isothermal degradation by TGA

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دراسة حركية الانحلال الحراري لمتعدد الستايرين باستخدام تقنية التحليل الحراري الوزني غير الثابت حرارياً

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المستخلص

أجريت دراسات الحركية للانحلال الحراري للبولي ستايرين من نوع (PS 120) المجهز من قبل شركة (Sabic) بواسطة التحليل الوزني الحراري باستخدام Flynn-Wall-Ozawa , Friedman, Kissinger , Coats-Redfern, dynamic, and Horowitz-Metzger عند خمسة معدلات تسخين 5,10,15,20,25 درجة مئوية/ دقيقة ضمن مدى حراري يتراوح 30-775 درجة مئوية ضمن محيط من الغاز الخامل (الهليوم) بسرعة جريان 20 مل/دقيقة . نتائج طاقة التنشيط المستحصلة تشير إلى أن انحلال السلسلة يتبع مسار الانحلال العشوائي . معدل طاقة التنشيط المستحصلة 230 كيلو جول/مول وهذه القيمة تتوافق بصورة جيدة مع القيم المنشورة .

Abstract

The kinetic analysis was carried out for thermal degradation by using of Thermo gravimetric analysis TGA analysis of polystyrene (PS 120) produced by Sabic company , using models of Flynn-Wall-Ozawa , Friedman, Kissinger , Coats-Redfern, dynamic, and Horowitz-Metzger methods. Activation energy was determined . The experiments were conducted at five heating rates of 5,10,15,20,25 C°/min. The temperature range of 30 - 775 C° under helium as inert gas was used with flow rate 20 ml/min . The obtained activation energy dependences are interrupted, the thermal degradation which follows random scission pathway, average activation energy obtained was 230 KJ/mol . This value was compared with published data and was found in a good agreement.

Introduction

One of the limiting factors in the application of plastics at high temperatures is their tendency to become softer, and degradable thermally. Thermal degradation can present an upper limit to the service temperature of the plastics and the possible loss of mechanical property. Significant thermal degradation can occurs at temperatures

much lower than those at which mechanical failure is likely to occur. Thermal degradation of polymers is molecular deterioration as a result of overheating. At high temperatures, the component of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the property of the polymer. In general, the ability of a plastic resistance to degradation called the stability. Therefore the thermal degradation of polymers has been investigated and become the centre of thermal analysis studies for many years^(1-5,17-19). Special interest on the degradation kinetics under inert and oxidative atmosphere performed. TGA was give to study the kinetics of polymer degradation. Kinetic analysis may effectively assist in the probing degradation mechanism as well as in the predicting the thermal stability of the polymer, therefore, the present paper is another attempt to describe such degradation kinetically.

Kinetic theory

According to the Flynn-Wall-Ozawa method⁽⁶⁻⁷⁾, which involves measuring the temperature corresponding to fixed value of α from experiments at different heating rates β , the activation energy, E at any particular value of α is determined by the following equation

$$\text{Log } \beta = \log\{A_0 \cdot E/R \cdot g(\alpha)\} - 2.315 - 0.4567(E/R \cdot T) \quad (1)$$

Where $g(\alpha)$ is the integral form of $f(\alpha)$, A_0 is pre-exponential factor and R is gas constant. Thus at a constant conversion the plot of $\log \beta$ vs. $1/T$, obtained from a series of experiments performed at several heating rates, should be a straight line whose slope allows evaluation of the activation energy.

$$\text{Slope} = d(\log \beta)/d(1/T) = -0.4567(E/R)$$

By using Friedman method⁽⁸⁾, which is based on the comparison of the rate of weight loss da/dt for a given conversion α by using different heating rates β :

$$\ln(da/dt) = \ln\{A_0 (1-\alpha)^n\} - E/R \cdot T \quad (2)$$

The value of E can be obtained from the slope $-E/R$ by plotting $\ln(da/dt)$ against $1/T$

When employing Kissinger method⁽⁹⁾, $\ln(\beta/T_m^2)$ is plotted against $(1/T_m)$ for a series of experiments at different heating rates β , with the peak temperature, T_m , obtained from the DTG, the slope which leads to $(-E/R)$ in the following Kissinger equation

$$\ln(\beta/T_m^2) = \ln(A_0 R/E) + (1/T_m)(-E/R) \quad (3)$$

The dynamic model⁽¹⁰⁾ becomes at the maximum degradation

$$\ln(\beta) = \ln(A_0) + (3/2) \ln T_m - \ln\{(E_m/R \cdot T_m) + (1/2)\} - \{E_m/(R \cdot T_m)\} \quad (4)$$

The plot of $\ln \beta$ versus $1/T_m$ should give a straight line with the slope determining the activation energy E_m at the maximum rate and $\ln A_0$ can be calculated from

activation energy and the intercept of y-axis. For the first order reaction, then the value of E at any conversion can be obtained from the following equation⁽¹¹⁾.

$$E = -R.T \ln[(d\alpha/dt) / (A_0 \{T^{1/2} (1-\alpha)\})] \quad (5)$$

The Coats-Redfern method is a multi-heating rate application of the Coats-Redfern equation⁽⁹⁾.

$$\ln\{-\ln(1-\alpha)/T^2\} = \ln(A_0 R / \beta E) \{1 - (2RT/E)\} - (E/RT) \quad (6)$$

By plotting $\ln\{-\ln(1-\alpha)/T^2\}$ against $1/T$ for each heating rate gives a family of straight lines of slope $-E/R$.

For first order reaction Horowitz-Metzger equation⁽⁹⁾ is

$$\ln\ln\{1/(1-\alpha)\} = E\theta/R.T_s^2 \quad (7)$$

where T_s is the temperature at which $(1-\alpha)=0.368$ and $\theta=T-T_s$. Thus a plot of $\ln\ln\{1/(1-\alpha)\}$ against θ allows to determine the activation energy.

Experimental

A commercial polystyrene (PS 125) produced by Sabic company was used in the present investigation. The thermo gravimetric measurement was carried out by a Perkin Elmer TGA analyzer, in non-isothermal condition. These experiments were carried out at Ibin Sina company (Ministry of Industry). The samples weights were (23.5, 23.99, 26.3, 26.8, 28.176 mg). Decomposition profiles were obtained while heating rates at 5, 10, 15, 20, 25 °C/min in Helium atmosphere with a flow rate of 20 ml/min between 30-775°C°. The sample mass was heated in a standard ceramic pan with temperature accuracy $\pm 0.2^\circ\text{C}$.

Results and discussion

Fig.(1) showed the (TG) curves of polystyrene (PS 125) under Helium atmosphere at different heating rates. However it can be seen the curves were displaced to higher temperatures because heat transfer lag at increased heating rates. For all samples residue less than 0.27 mg were observed, based on sample weight 23.5-28.176 mg. Therefore, it be concluded that nearly all of material subjected to degradation was transformed to volatile material. The typical TG and DTG under Helium atmosphere at a heating rate of 25 °C/min are shown in Fig. 2.

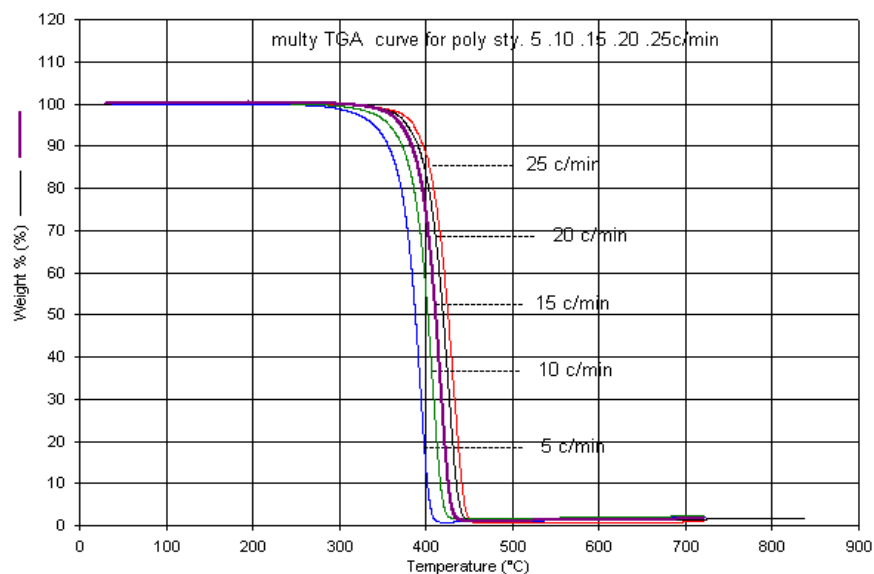
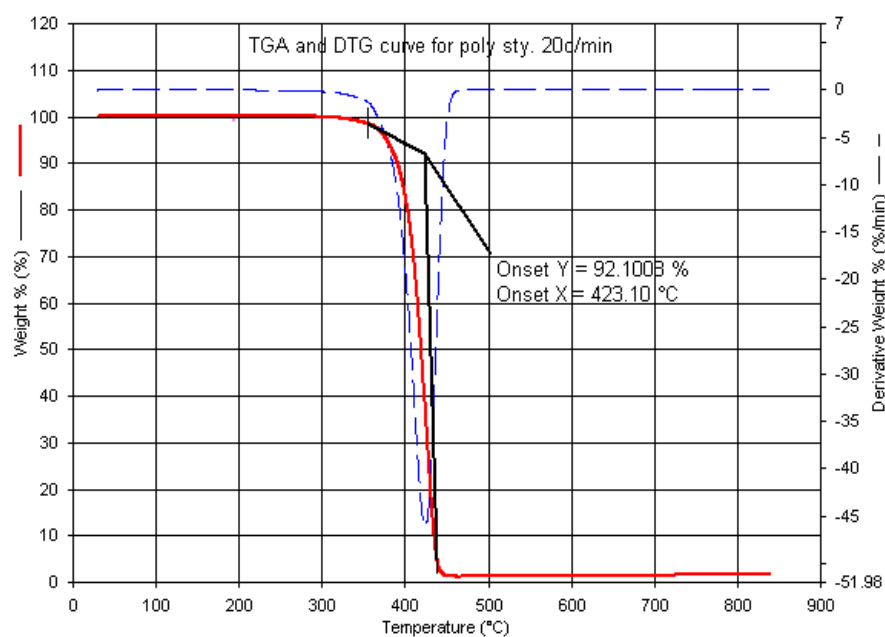


Figure (1): TGA curves recorded under Helium atmosphere at various β



Figure(2): TGA and DTG curve recorded under Helium atmosphere at $\beta = 25$ $^{\circ}\text{C}/\text{min}$

The activation energy has been estimated by employing Flynn-Wall-Ozawa, Kissinger, Coast-Redfern, Friedman, dynamic, and Horowitz-Metzger methods. However the activation energy was found by Flynn-Wall-Ozawa and Friedman method are fairly lower than other method ⁽¹⁻⁷⁾. Table 1 showed the numerical data extracted from Fig 1 as well as activation energy estimated by Flynn-Wall-Ozawa and Friedman methods. By using Ozawa method, a series of straight lines can be

constructed by plotting $\log \beta$ vs. $1/T$, the activation energy for each conversion level can be determined from the slope as shown in Fig 3.

Also by Friedman method a series of straight line can be obtained by plotting $\ln(d\alpha/dt)$ vs. $1/T$, the activation energy can be obtained for each reaction rate level.

The results in Table 1 emphasize that the activation energy are slightly affected by different heating rates, and its magnitude are fairly lower than the other method.

Table (1): Numerical data of thermal degradation at different level of β

(1- α)	T, K $\beta = 5$ C°/min	T, K $\beta = 10$ C°/min	T, K $\beta = 15$ C°/min	T, K $\beta = 20$ C°/min	T, K $\beta = 25$ C°/min	E, KJ/mol Ozawa method	E, KJ/mol Friedman method
0.1	675.4	691.0	701.2	709.0	715.0	154.88	---
0.2	670.6	686.2	697.0	704.2	711.4	149.37	141.89
0.3	669.4	682.2	694.6	700.0	706.6	159.47	149.21
0.4	664.6	679.0	688.6	695.8	703.0	156.21	146.37
0.5	661.0	674.6	685.0	691.0	698.8	156.96	149.55
0.6	656.2	671.2	681.4	686.6	694.6	153.65	145.08
0.7	651.4	665.8	676.4	680.2	689.8	152.55	142.98
0.8	643.0	658.6	669.4	673.0	682.0	146.24	149.64
0.9	634.6	646.6	656.2	662.2	670.0	154.15	142.78
E (1- α) 0.1-0.9						153.72	145.93

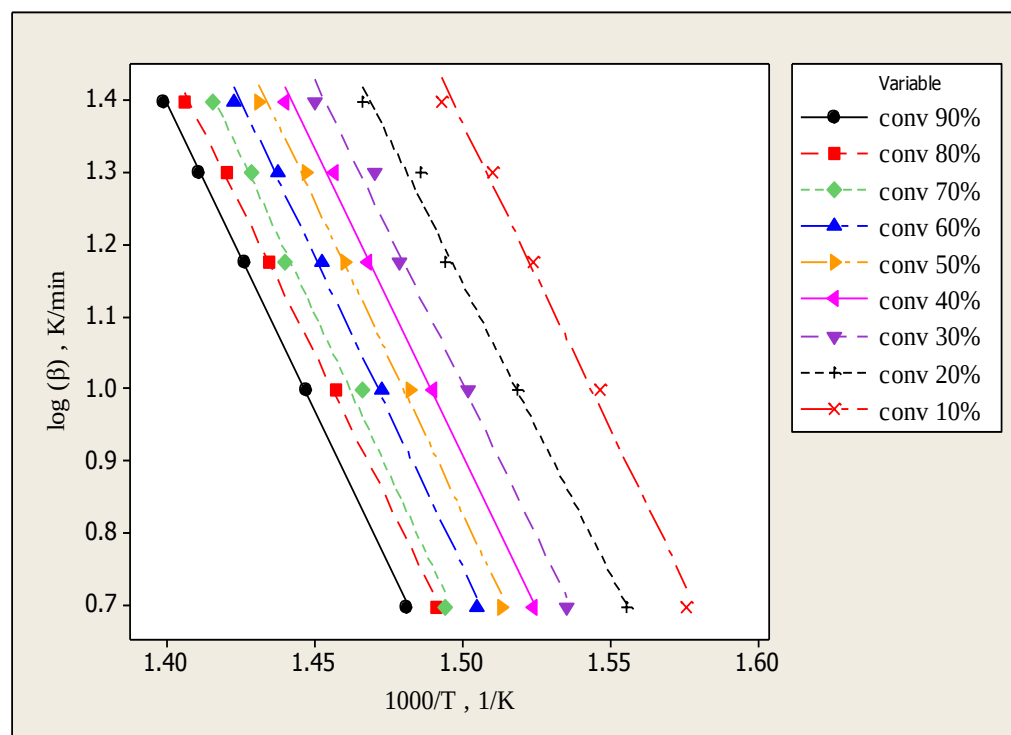


Figure (3): plot $\log \beta$ vs. $1/T$ of constant conversion

The Kissinger's plot exhibited a good linear relationship indicating that the Kissinger's was effective in describing the thermal decomposition kinetics. The activation energy calculated from the slope of the plot are given in Fig 4

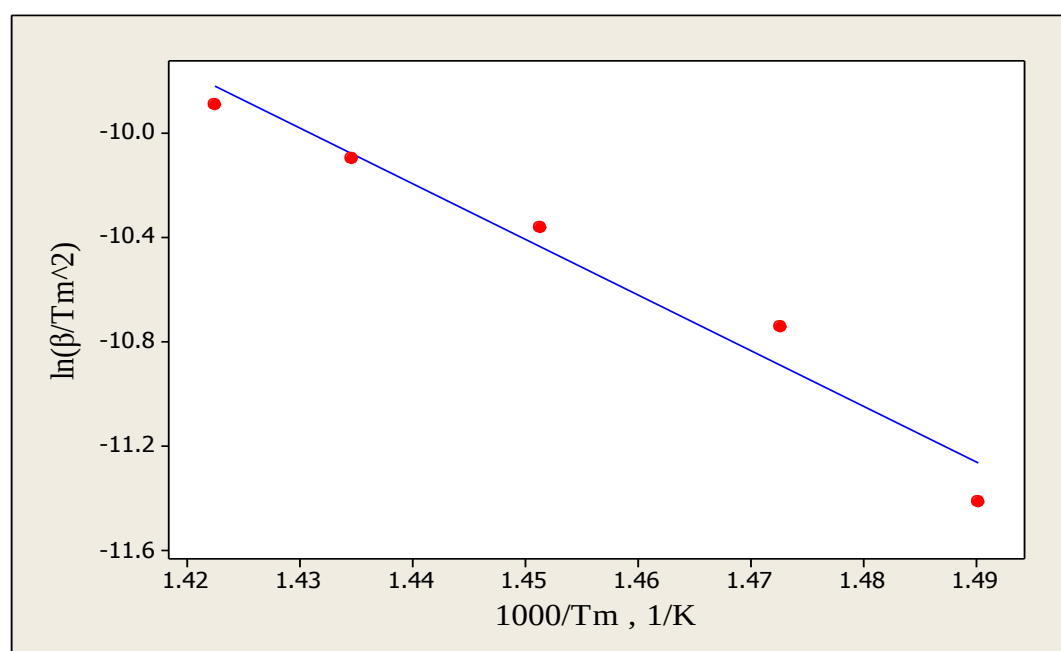


Figure (4): Plot $\ln(\beta/T_m^2)$ vs. $1/T$ for determining kinetics data

Fig 5 showed the plot $1/T_m$ against $\ln \beta$ according to dynamic method employed to determine the factor A_0 . However the plot are straight lines having slope equal $-E_m/R$, thus the activation energy E_m can be obtained at maximum degradation rate. The values of A_0 are obtained by substituting E_m back in the intercept, the results are summarized in the Table 2. The activation energies upon conversion obtained from A_0 and equation 10, and TGA data by Dynamic method are shown in Fig. 6. A slight variation observed in activation energy when using various heating rates, therefore it can be concluded that these results are slightly affected by the heating rates.

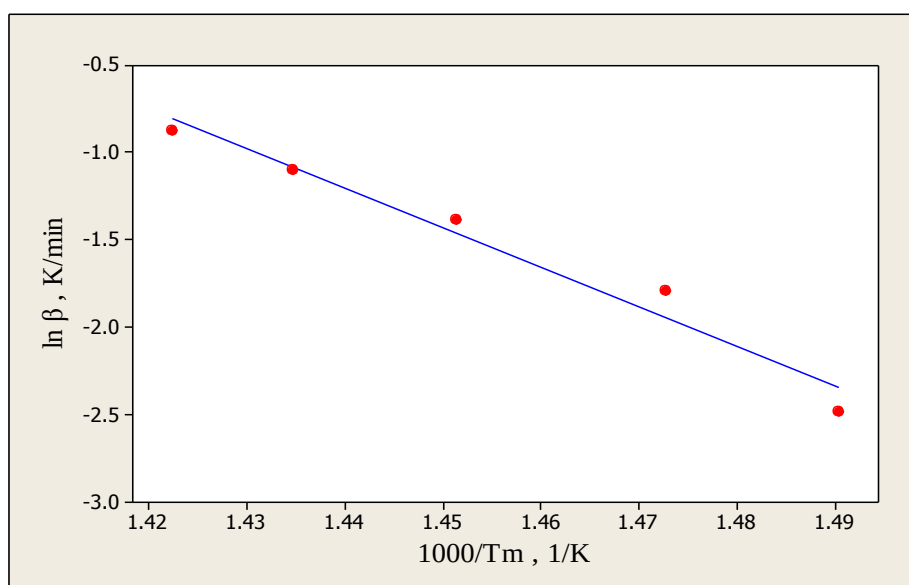


Figure (5): Plot of $\ln \beta$ vs. $1/T$ according to Dynamic method

Table 2: Determination of kinetics data by Dynamic method

Heat rate β (C°/min)	Onset temperature,(K)	Peak temperature, T_m (K)	Activation energy, E_m (kJ/mol)	Factor, A_0 (S ⁻¹ K ^{1/2})
5	666.6	671.0	183.14	0.34500×10^{11}
10	678.6	679.0		0.33499×10^{11}
15	689.0	689.0		0.32305×10^{11}
20	696.1	697.0		0.31391×10^{11}
25	703.0	703.0		0.30247×10^{11}

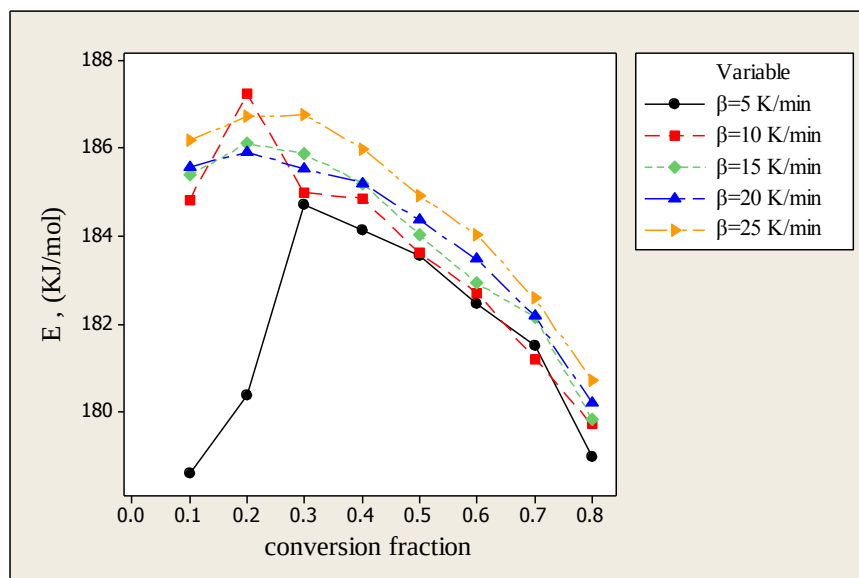


Figure (6): Activation energy upon conversion according to dynamic method

According to Coast-Redfern method Fig. 7 showed strong linear relationship which describes thermal degradation very strongly.

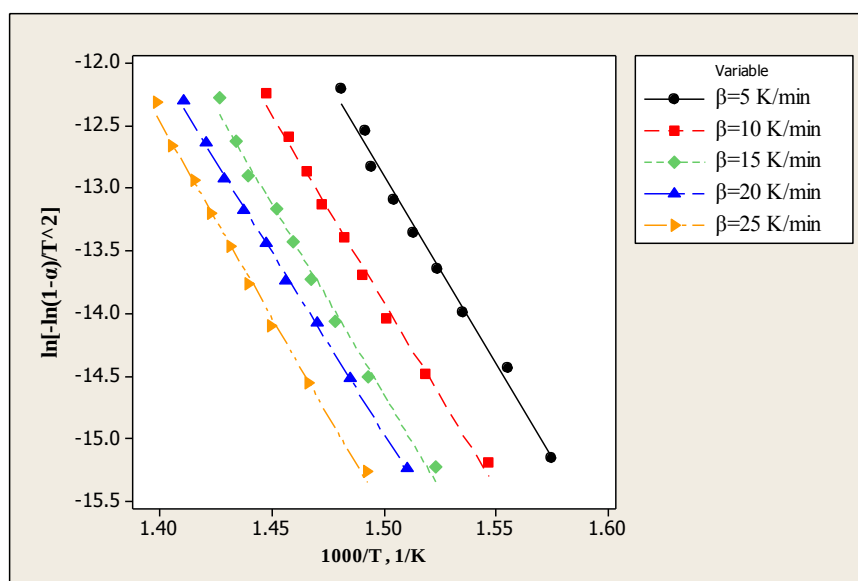


Figure (7): Coast-Redfern plot for thermal degradation at different β

The same trend was observed in Horowitz-Metzger's method as shown in Fig. 8 which describes also more effectively the degradation reaction.

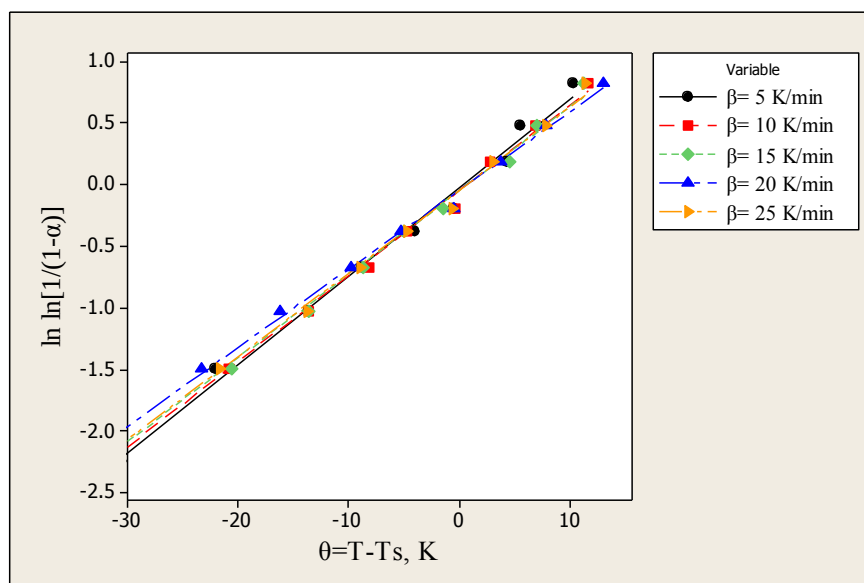


Figure (8): Horowitz-Metzger's plot for thermal degradation at different β

Fig. 9 showed the effect of different heating rate on activation energy for Dynamic, Coast-Redfern, and Horowitz-Metzger models. However it concluded that, the use of multiple heating rate method represented more realistically the verity of heating rate used for thermal degradation of polymers because of the wide variation obtained when using various heating rates.

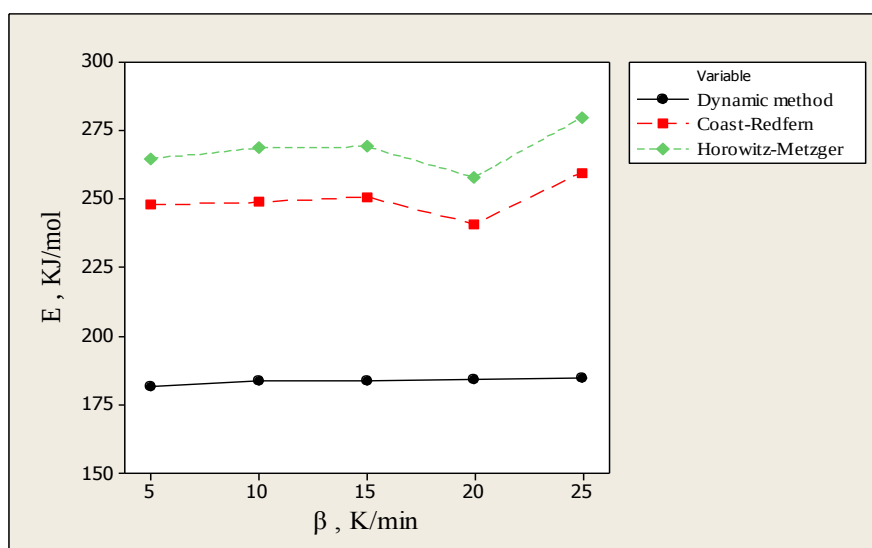


Figure (9): Comparison of activation energy obtained by different method

For comparative purpose the results are summarized in Table 3. The kinetic parameters obtained by models represented in Fig. 9 are more reasonable in describing the degradation process and are in a good agreement with published data as shown in Table 4. However it can be seen from Table 3, there is tremendous variation in activation energy depending on used model. Also, this observation explained how the problem of selecting and utilizing different analytical technique for thermal degradation of polystyrene will be affected the kinetic results.

Table (3): Activation energy obtained by using different analytical method

Heating rate, β (C°/min)	Dynamic method E,(KJ/mol)	Coast-redfern method E,(KJ/mol)	Horowitz-Metzger method E,(KJ/mol)	Friedman method E,(KJ/mol)	Ozawa method E,(KJ/mol)	Kissinger Method E,(KJ/mol)
5	181.79	248.04	264.79	145.93	153.72	177.00
10	183.64	248.89	268.64			
15	183.94	250.93	269.20			
20	184.06	240.99	258.01			
25	184.74	259.77	279.89			

Table (4): Activation energies reported in the literature for thermal degradation of polystyrene

Authors	E, KJ/mol
Guoxi,X.,et al ⁽¹¹⁾	250
Marcilla,A.,et al ⁽¹²⁾	203-218
Marcilla,A.,et al ⁽¹²⁾	220-277
Dickenes,A.,et al ⁽¹³⁾	188
Tripathi,C.L.,et al ⁽¹⁴⁾	322
Lin,R., et al ⁽¹⁵⁾	203
Kuljanin Jakovljevic,J, et al ⁽¹⁶⁾	90-100

Conclusions

The Dynamic, Coast-Redfern, Horowitz-Metzger, and Kissinger methods have yielded dependencies of effective activation energy on the extent of polystyrene thermal degradation that agrees very strongly with data published. Therefore we believe that our approaches are the best methods for kinetic analysis of thermal degradation of polystyrene compared to Ozawa, and Friedman methods which predicted lower activation energy. The values of activation energy of the three models

don't vary highly than the other methods. These values suggest that the degradation of polystyrene as a single reaction. These results are in agreement with the other investigators of degradation initiated by weak link sites⁽¹⁷⁾ which also mentioned that the major mass loss of polymer occurs due to the random scission process.

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