Thermogravimetric Analysis of Polystyrene: Influence of Sample Weight and Heating Rate on Thermal and Kinetic Parameters

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SYNOPSIS

This article studies the influence of the heating rate and sample weight on the thermal decomposition of polystyrene (first-order kinetics). For this purpose, the kinetic parameters (i.e., frequency factor and activation energy), variables at the maximum decomposition rate (such as conversion, reaction rate, and temperature), as well as some characteristic temperatures have been determined for a series of experiments where the heating rate varies (0.5–11.5 K/min) and also, the sample weight (6.0–25.1 mg). Some mathematical equations have been developed that allow: (1) evaluation of the activation energy of thermal decomposition by different ways and comparing the results obtained; (2) relating different parameters between themselves, such as the heating rate with the temperature at the maximum decomposition rate or the frequency factor with the heating rate and sample weight. Finally, some theoretical explanations of the variation of thermal and kinetic parameters have been proposed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The thermal decomposition of polymeric materials can be studied by means of dynamic thermogravimetry (with a linear temperature increase). This technique is useful to elucidate the order of reaction, to estimate kinetic parameters such as the activation energy and the frequency factor, to evaluate the rate of decomposition, as well as some thermal parameters such as the temperature at the maximum decomposition rate and characteristic temperatures. The greater precision of experimental values obtained from TG in comparison with DTA and DSC is attributable to the accuracy in measurement of weight.[1]

The advantages of determining kinetic parameters by nonisothermal methods rather than by conventional isothermal studies are the following: (1) the kinetics can be established over an entire temperature range in a continuous manner; (2) it is possible to obtain a lot of information with a single sample (i.e., thermal parameters such as temperature at the maximum decomposition rate, characteristic temperatures, and kinetic parameters); (3) the determination of kinetic and thermal parameters using a single sample eliminates problems arising from different samples (i.e., sample-to-sample error is avoided); (4) when a sample undergoes considerable reaction in being raised to the required temperature, the results obtained by isothermal methods are questionable because some degradation may occur during the preheating period, particularly when the temperature of the onset of reaction is considerably lower than the temperature of isothermal trials.

Mathematical modeling of thermal decomposition reactions helps to understand the process being studied, checking the validity of assumptions and deducing quantitative conclusions from apparent kinetic parameters. The latter is essential to achieve engineering calculations leading to the determination of the reactor size. The literature[2-20] mentions great variations in the activation energy of the ther-

mal decomposition of polystyrene (Table I), taking values between 90 and 290 kJ/mol. These differences depend on several factors: (1) preparation method of the polymer (i.e., anionic, thermal, or other type of polymer preparation; lattice defects; weak links; impurities)[14,21] as well as the particle size. (2) Molecular weight of the polymer[5,18,22-24]. (3) Operating conditions, i.e., sample weight, sample particle size, heating rate, mass flow and type of gas, thermal contact between sample and sample holder, etc.[1,25] (4) Mathematical treatment of thermogravimetric data following different computing methods (integral, differential, and special).[20,26-27] For example, Carrasco[20] has shown that the application of different computing methods to the same TG data resulted in activation energy values varying from 102 to 152 kJ/mol (integral methods), 126–143 kJ/mol (differential methods), and 106–140 kJ/mol (special methods).

The objectives of this article are: (1) to evaluate the kinetic parameters as well as the characteristic temperatures representing the thermal decomposition of polystyrene under different operating conditions. (2) To determine the conversion and temperature at the maximum rate of decomposition. (3) To quantify the influence of procedural factors, such as the sample weight and heating rate, on kinetic parameters and characteristic temperatures. In order to avoid variations arising from other variables, the same sample of polystyrene (i.e., constant molecular weight, particle size, compactness, etc.) was used through all the experimentation. In addition, all the TG trials were carried out in the presence of air flowing at the same pressure and mass flow rate. Finally, TG data were processed by using the same integral method to avoid differences related to the type of computing method (i.e., integral, differencial, or special methods).

Table I Values of the Activation Energy Found in the Literature for the Thermal Decomposition of Polystyrene

E, kJ/mol	Remarks	Reference
163	270–320°C. Chain scission. No volatilization	Boon and Challa, 1965
175	290–330°C. Isotactic PS	Nakajima et al., 1966
187	In vacuum. f = 15–80%. Independent of M_w	Jellinek, 1949
230	Maximum rate method. $T \sim 350°C$	Wall et al., 1966
200	In absence of O_2. 250–301°C	Wegner and Patat, 1970
180	Isothermal	Still and Whitehead, 1976
188 ± 1	$T > 350°C$. In vacuum or in flowing N_2 (nonoxidative)	Dickens, 1980
90 ± 1	$T > 280°C$. In an atmosphere of abundant O_2 (oxidative)	
146 ± 1	$f < 0.3$ (n = 0). 50 mg, 2°C/min (N_2)	Coats and Redfern, 1965
192	$f < 0.4$ (n = 0)	Anderson and Freeman, 1961
250	$f > 0.5$ (n = 1)	
272	f = 0.15–1 (n = $\frac{1}{2}$) (N_2)	Vovelle and Mellotée, 1983
215–227	In vacuum. Anionic PS. 5–15°C/min, 1–2 mg	Mehmet and Roche, 1976
	Random chain scission. 280–300°C	Cameron and McWalter, 1982
204 ± 8	In vacuum	
191 ± 8	In 0.5 atm air	
133 ± 8	In 1 atm O_2	
	Negligible formation of volatiles	Cameron and Kerr, 1970
209	Thermal PS	
272	Anionic PS	
230		Madorsky, 1964
188–213	Anionic PS. M_w = 5,300–48,000	Wall et al., 1973
180	300–400°C, Isothermal, f = 0.1–0.95 $(df/dT)_{max}$ at f = 0.15–0.30	Bouster et al., 1980
140	$f < 0.4$ (n = 0)	Kokta et al., 1973
210	$f < 0.5$ (n = 1)	
	5 mg, 10°C/min, n = 1	Nishizaki et al., 1980
190–290	Depending on computing method employed	
102 ± 12–152 ± 1	6–7 mg, f = 0.03–0.85, 0.5–12 K/min, 0.8 < n < 1.3	Carrasco, 1993
	Depending on computing method employed	

EXPERIMENTAL

Samples were obtained from Scientific Polymer Products (anionic preparation and polydispersity below 1.06). The substance used in this study was a white powder with a molecular weight of M_w = 7800 g/mol. The thermal decomposition of polystyrene samples was carried out in a thermal analyzer (Netzsch, Gerätebau Model STA 409). Operating conditions were the following: heating rate = 0.50–11.50 K/min and sample weight = 6.0–25.0 mg. Degradations were conducted at atmospheric pressure and gases produced by decomposition were swept out by a flow of air at 100 mL/min.

RESULTS AND DISCUSSION

As previously indicated, the activation energy depend on the molecular weight. In general, the activation energy increases with the molecular weight and reaches an asymptotic value at high molecular weigths.[5,16,18,23] However, there is an important dispersion due to the different nature of the polystyrene used in each work. This means that the particle diameter, compactness, and chemical nature of the polystyrene is also an important factor to be considered. In order to study the influence of procedural factors (i.e., sample weight and heating rate), the same sample of polystyrene was always used.

Similarly, it is important to use the same computing method to avoid divergences due to mathematical calculations. Therefore, the integral method developed by Carrasco,[20] which gives the general solution for the thermal decomposition of solids, has been applied. Because the thermal decomposition of polystyrene follows a first order kinetics, the general solution becomes:

$$f = 1 - \exp\left(- \frac{ART^2}{\beta E}\left[\exp\left(- \frac{E}{RT}\right)\right]\right.$$
$$\left. \times \sum_{i=1}^{\infty} (-1)^{i+1} i! \left(\frac{RT}{E}\right)^{i-1}\right), \quad (1)$$

where:

A: frequency factor, s^{-1}
E: activation energy, kJ/mol
f: conversion
R: gas constant, 8.315 J/mol·K
t: time, s

T: temperature, K
β: heating rate, $K \cdot s^{-1}$

The sum can be truncated at the second term (i = 2) if the thermal energy (RT) is significantly less than the activation energy (E). Conversion is, therefore, expressed as follows:

$$f = 1 - \exp\left[- \frac{ART^2}{\beta E}\left(1 - \frac{2RT}{E}\right)\exp\left(- \frac{E}{RT}\right)\right]. \quad (2)$$

The first and second conversion derivatives are readily obtained by taking into consideration the previous rate equation. Because the maximum rate of decomposition is reached when $d^2f/dT^2 = 0$, the activation energy can be readily evaluated:

$$E = RT_m^2 \frac{\left(\dfrac{df}{dT}\right)_m}{(1 - f_m)}. \quad (3)$$

The best order was chosen by means of analysis of variance (ANOVA) and resulted to be one (pseudofirst-order kinetics) in all the experiments. Kinetic parameters, as shown in Table II, were obtained by linear regression of eq. (2). These results clearly indicate that kinetic parameters vary with the sample weight (w_o) and heating rate (β). Figure 1 shows that the activation energy is invariable (average value of = 128.7 kJ/mol) at low values of $\beta \cdot w_o$. In other words, when small samples are decomposed at low or moderate heating rates, the reaction mechanism remains the same and there is no mass/thermal effects as evidenced by constant activation energy values. However, when large samples are heated rapidly (i.e., high values of $\beta \cdot w_o$), apparent activation energy increases (146–162 kJ/mol), thus indicating either a mechanism change or some problems related to heat and/or mass transfer. When a thermal decomposition takes place, the diffusion of heat and/or decomposition gases have to be considered as a simultaneous process to chemical reaction. The endothermal/exothermal reaction induces an inhomogeneous temperature distribution. On the other hand, although constancy of heating rate in TG is generally supposed when using a linear heating program, the heating rate is perturbed in the sample when reaction is taking place. Small samples and low heating rate reduce this influence. Moreover, partial pressure of gas gives rise to partial reverse reaction. By performing the experiments at low pressure, the influence of reverse reaction may dras-

tically be reduced (but there is lower heat exchange in high vacuum). As stated by Várhegyi,[21] the pressure effect can be reduced by using small samples. Another way to reduce reverse reactions, but without lowering heat exchange, is by using flowing air in order to evacuate volatilization products as they are formed, as in our experimental conditions (flow of air at atmospheric pressure). In order to meet the ideal conditions as far as possible, the use of small samples and low heating rates have been recommended.[28,29] Our experimental results of activation energy confirm this assertion.

Operating conditions leading to the same activation energy have been selected to study the variations of the frequency factor due to procedural factors. If the activation energy changes, the variation of the frequency factor could be attributed to a compensation effect between both variables. By using linear regression, the following simple empirical expressions were obtained:

At constant heating rate, β = 1.0 K/min (samples 2, 3, 6, and 7):

$$A = 5.39 \times 10^8 \, w_o^{-0.63} \quad (r^2 = 0.996). \quad (4)$$

At approximately constant sample weight, w_o = 6.2–6.7 mg (samples 1 to 5):

$$A = 1.69 \times 10^8 \beta^{-0.19} \quad (r^2 = 0.991), \quad (5)$$

where A is expressed in s^{-1}, β in K/min, and w_o in mg.

These equations clearly indicate that the frequency factor decreases when increases the sample weight and the heating rate. This result is, again, supporting the hypothesis proving the importance of the matrix and diffusion effects during the thermal
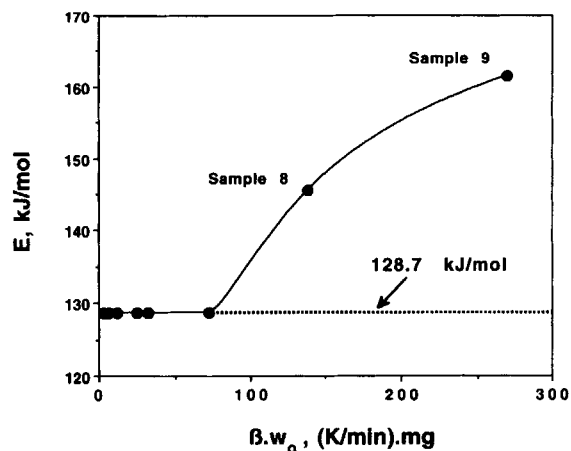

Figure 1 Influence of procedural factors (expressed as the product $\beta \cdot w_o$) on activation energy values.

decomposition of solids. The exponent of the independent variable (either sample weight or heating rate) indicates that the frequency factor is more influenced by the sample weight than the heating rate. The reduction of the frequency factor when increasing the sample weight can be attributed to a "cage effect": the gaseous molecules formed during the thermal decomposition are trapped by the solid matrix, thus generating a recondensation/volatilization equilibrium. This effect obviously reduces the rate of decomposition, which can be related to a decrease in the frequency factor.

Two characteristic temperatures have been derived from the weight loss curves. As illustrated in Figure 2, the characteristic temperature T_{c0} is obtained from the TG curve as the value of the intercept between the locus of $f = 0$ and the tangent line at the maximum rate of decomposition. On the other hand, the characteristic temperature T_{c1} is obtained

Table II Variation of Kinetic Parameters as a Function of Procedural Factors (Heating Rate and Sample Weight)

Sample	β, K/min	w_o, mg	E^a, kJ/mol	A, s^{-1}	r^2
1	0.5	6.7	128.6 ± 0.8	1.97 × 10⁸	0.996
2	1.0	6.2	128.6 ± 0.4	1.68 × 10⁸	0.999
3	1.0	6.4	128.7 ± 0.7	1.65 × 10⁸	0.997
4	5.4	6.0	128.7 ± 1.4	1.27 × 10⁸	0.991
5	11.5	6.3	128.7 ± 0.7	1.06 × 10⁸	0.997
6	1.0	12.4	128.6 ± 0.9	1.14 × 10⁸	0.995
7	1.0	25.0	128.7 ± 0.2	0.69 × 10⁸	1.000
8	5.5	25.1	145.5 ± 0.7	13.4 × 10⁸	0.998
9	10.8	25.0	161.5 ± 0.8	235.4 × 10⁸	0.998

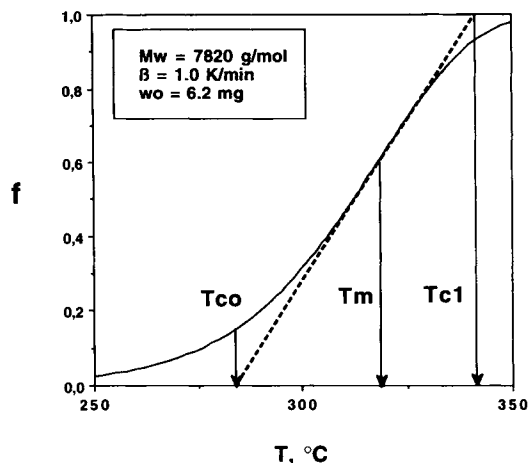[a] The confidence interval was calculated at 95% confidence level.

Figure 2 Mathematical evaluation of the characteristic temperatures T_{c0} and T_{c1}.

from the TG curve as the value of the intercept between the locus of $f = 1$ and the tangent line at the maximum rate of decomposition. These temperatures are mathematically expressed as follows:

$$T_{c_0} = T_m - \frac{f_m}{\left(\dfrac{df}{dT}\right)_m} \tag{6}$$

$$T_{c_1} = T_m + \frac{(1 - f_m)}{\left(\dfrac{df}{dT}\right)_m} . \tag{7}$$

From eqs. (6) and (7) it is possible to find out the difference of characteristic temperatures, $\Delta T_c = T_{c1} - T_{c0}$, which corresponds to the inverse of the maximum rate of decomposition:

$$\Delta T_c = \frac{1}{\left(\dfrac{df}{dT}\right)_m} . \tag{8}$$

Table III contains the values of temperature, conversion, and conversion derivative at the maximum rate of decomposition for a set of experiments having as varying parameters the heating rate and the sample weight. Table IV shows the excellent reproducibility for the experiments carried out in this study. Figure 3 illustrates the excellent correlation existing between the difference of characteristic temperatures and the inverse of conversion derivative at the maximum decomposition rate, also meeting the terms of eq. (8). It is easily perceptible that the experimental value of the slope (0.993) only differs 0.7% from the theoretical value, which is equal to the unity. Also to be noticed is that the correlation is maintained independent from the activation energy values (128.7 kJ/mol for Experiments 1 to 7, 145.5 kJ/mol for Experiment 8, and 161.5 kJ/mol for Experiment 9). This means that independently from the reason why the activation energy varies (either change of reaction mechanism or limitations due to the heat transfer or mass diffusion), the above-indicated relation is maintained. On the other hand, when only considering experiments (points 1 to 7) that correspond to constant activation energy of 128.7 kJ/mol, an increase of the heating rate (at constant sample weight) is observed to cause an increase of both the difference of characteristic temperatures and the conversion derivative. Similar conclusion have been drawn on increasing the sample weight (at a constant heating rate). With regard to the experiments with different activation energy (points 8 and 9), they are observed

Table III   Variation of Thermal Parameters as a Function of Procedural Factors (Heating Rate and Sample Weight)

Sample	β, K/min	w_o, mg	T_m, K	f_m	$10^2 \, (df/dT)_m$, K^{-1}	T_{c0}, K	T_{c1}, K	ΔT_c, K
1	0.5	6.7	574.3	0.606	1.847	541.5	595.6	54.1
2	1.0	6.2	592.2	0.612	1.743	557.1	614.2	57.1
3	1.0	6.4	592.4	0.606	1.740	557.6	615.1	57.5
4	5.4	6.0	629.5	0.604	1.547	590.5	655.1	64.6
5	11.5	6.3	659.6	0.603	1.414	617.0	687.7	70.7
6	1.0	12.4	600.2	0.605	1.696	564.5	623.5	59.0
7	1.0	25.0	611.5	0.606	1.637	574.5	635.6	61.1
8	5.5	25.1	657.5	0.606	1.596	619.5	682.2	62.7
9	10.8	25.0	675.7	0.608	1.700	639.3	699.2	59.9

Table IV Reproducibility Results

w_o, mg	β, K/min	E, kJ/mol	10^{-8} A, s^{-1}	T_m, K	f_m	10^2 $(df/dT)_m$, K^{-1}	T_{c0}, K	T_{c1}, K
6.2	1.0	128.6	1.6797	592.2	0.612	1.743	557.0	614.4
6.4	1.0	128.7	1.6518	592.4	0.606	1.740	557.6	615.0
Relative error, %		0.08	1.7	0.03	1.0	0.2	0.1	0.1

to be randomly distributed—even though following the correlation—which could implicate a compensation effect similar to the well-known one existing between the activation energy and the frequency factor.

By rearrangement of eq. (3), the activation energy can be determined by linear regression:

$$\frac{(1 - f_m)}{\left(\dfrac{df}{dT}\right)_m} = \frac{R}{E} T_m^2 . \tag{9}$$

Figure 4 gives evidence of the excellent correlation of the experiments corresponding to constant activation energy (points 1 to 7). From the slope, an activation energy equal to 127.3 kJ/mol has been calculated, a value that is very close to the one assessed by linear regression of the general equation [eq. (2)]. The higher the activation energy, the more points 8 and 9 separate from the straight line. Therefore, this type of representation can detect if the experimental points of experiments performed at different heating rates and/or sample weights meet the condition of constant activation energy.
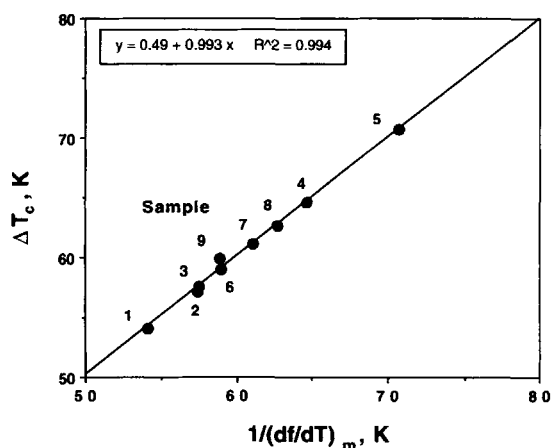
By combining eqs. (3) and (8), a relationship between characteristic temperature differences and temperatures at the maximum rate of decomposition is obtained:

$$\Delta T_c = \frac{R}{E} \frac{1}{(1 - f_m)} T_m^2 . \tag{10}$$

It is worth noticing that this equation does not contain the conversion derivative, which is an advantage, as its determination usually gives rise to some imprecisions. Only the difference of characteristic temperatures with the temperature at the maximum decomposition rate are related in this equation. In Figure 5, ΔT_c has been represented as a function of $T_m^2/(1-f_m)$ [eq. (10)], and it shows an excellent straight line for the experiments giving a constant activation energy (points 1 to 7), something that was expected as the slope is equal to R/E. From the regression line, the activation energy value has been evaluated in 127.5 kJ/mol, which is similar to the one estimated (128.7 kJ/mol) by linear regression of the general equation [eq. (2)]. The higher the activation energy, the more the points 8
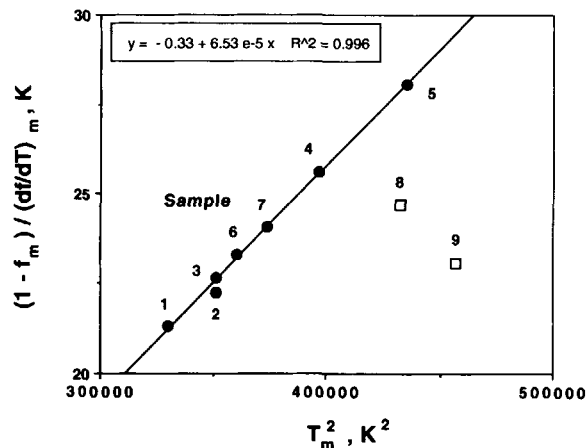

Figure 3 Variation of the difference of characteristic temperatures as a function of the inverse of conversion derivative at the maximum decomposition rate [regression analysis of eq. (8)].

Figure 4 Variation of $(1-f_m)/(df/dT)_m$ as a function of the square of temperature at the maximum decomposition rate [regression analysis of eq. (9); points 8 and 9 were not considered in the regression].
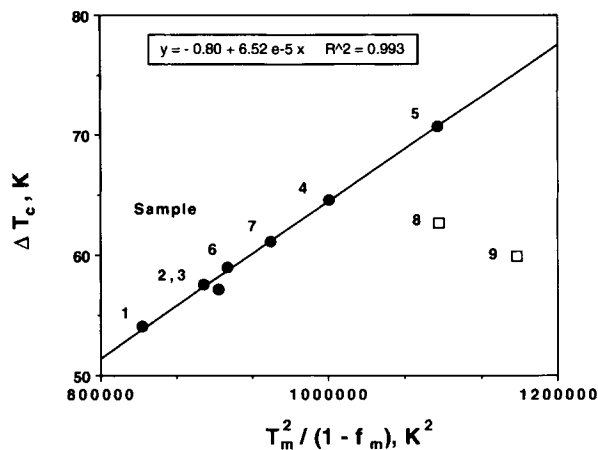
Figure 5   Variation of the difference of characteristic temperatures as a function of $T_m^2/(1-f_m)$ [regression analysis of eq. (10); points 8 and 9 were not considered in the regression].
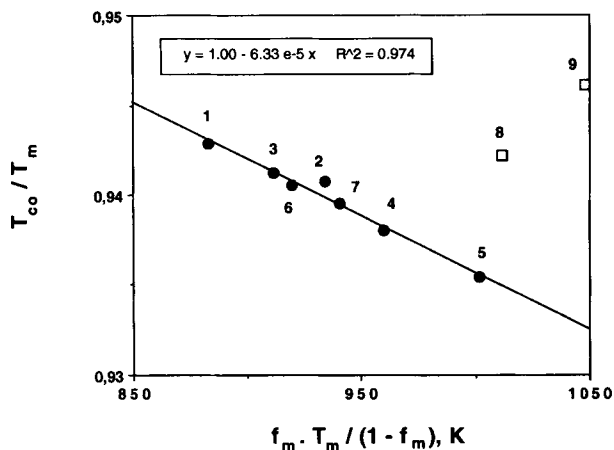

Figure 6   Variation of the temperature ratio T_{c0}/T_m as a function of $f_m \cdot T_m/(1-f_m)$ [regression analysis of eq. (11); points 8 and 9 were not considered in the regression].

and 9 separate from the straight line, as mentioned before for eq. (9).

By combining eqs. (6) and (9) or, alternatively, eqs. (7) and (9), the following expressions are obtained:

$$\frac{T_{c0}}{T_m} = 1 - \frac{R}{E}\frac{f_m}{(1-f_m)}\,T_m \qquad (11)$$

$$\frac{T_{c1}}{T_m} = 1 + \frac{R}{E}\,T_m\,. \qquad (12)$$

Equation (11) establishes a relation between the characteristic temperature T_{c0} and the temperature at the maximum decomposition rate. Figure 6 illustrated the excellent adjustment of the experimental points (1 to 7) to eq. (11). From this slope, the activation energy has been evaluated and found to be 131.4 kJ/mol, slightly higher value than the one calculated by linear regression of the general equation [eq. (2)]. In the same manner, Figure 7 illustrates the points fitted to eq. (12) with an activation energy of 122.2 kJ/mol, a slightly lower value than the evaluated one (128.7 kJ/mol) by linear regression of the general equation [eq. (2)].

By combining the derivative of eq. (2) and eq. (9), an expression is obtained relating the heating rate and the temperature at the maximum decomposition rate.

$$\ln \beta = \ln\!\left(\frac{ART_m^2}{E}\right) - \frac{E}{R}\frac{1}{T_m}\,. \qquad (13)$$

In fact, this equation is a theoretical explanation of the correlation proposed by Mehmet and Roche,[12] who assured the existence of a linear relation between $\ln \beta$ and $1/T_m$. In effect, Figure 8 does corroborate the existence of the indicated relation. It should be kept in mind that the straight line was obtained by linear regression of the full circular points as they correspond to Experiments 1 to 5, in which the sample weight is almost constant (6.0–6.7 mg), thus preventing the differences that may derive from a variation of the sample weight (i.e., effects of mass diffusion and heat transfer, as it has been mentioned before). It is, therefore, manifest that points 6 and 7 (corresponding to more bulky
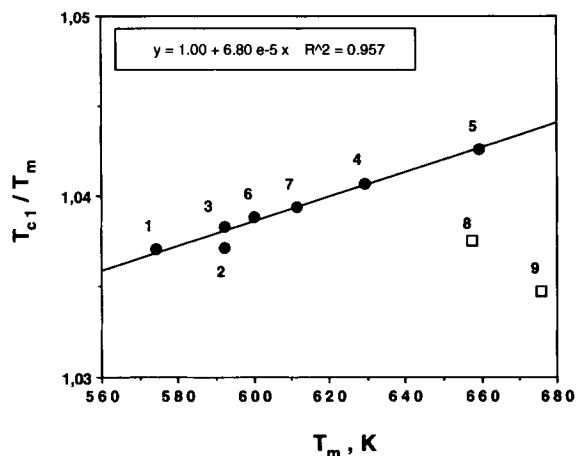

Figure 7   Variation of the temperature ratio T_{c1}/T_m as a function of temperature at the maximum decomposition rate [regression analysis of eq. (12); points 8 and 9 were not considered in the regression].
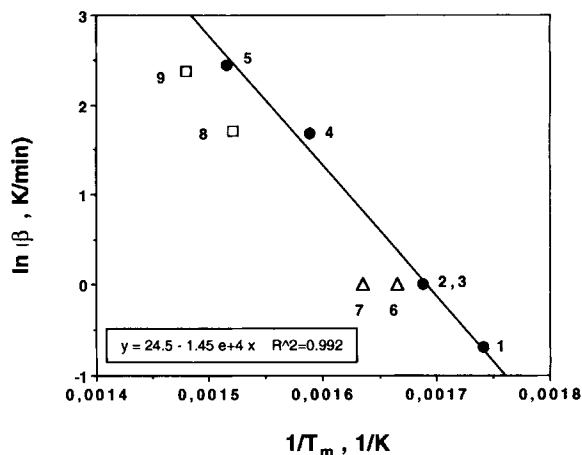
Figure 8 Influence of the inverse of temperature at the maximum decomposition rate on the logarithm of heating rate [regression analysis of eq. (13); points 6, 7, 8, and 9 were not considered in the regression].

samples)—even though belonging to experiments with the same activation energy as points 1 to 5—do not follow the behavior established by the straight line. This means that the intercept is lower than expected (i.e., lower frequency factor), thereby corroborating the thesis of a "cage effect" caused by larger samples. Because points 8 and 9 correspond to experiments with higher activation energy, it is logical that they do not adjust to the straight line as the slope ($-E/R$) should be steeper. On the other hand, Figure 9 shows the product $A \cdot T_m{}^2$ to be constant, and, hence, the intercept of eq. (13) is constant, *sine quanom* condition to be considered as a straight line. This result provides, in addition, some useful information, as it is evident that there is a compensation effect between the frequency factor and the square of temperature at the maximum decomposition rate for experiments with both constant activation energy and sample weight.

Because the sample weight is not present in any of the theoretical equations—the decomposition kinetics being of first order—empirical correlations have to be used to analyze the combined influence of the heating rate and sample weight. Equations (4) and (5) were used to evaluated the influence of the heating rate at constant sample weight and the influence of the sample weight at constant heating rate on the frequency factor. A unique expression considering the combined influence of both these variables could not be attained. It has been possible, though, to find correlations allowing the prediction of the combined effect of heating rate and sample weight on temperature at the maximum decompo-

sition rate and characteristic temperatures. For this purpose, a multiple linear regression analysis has been carried out. The resulting expressions are as follows:

$$T_m = 565.5 \; \beta^{0.043} w_o^{0.024} \quad (r^2 = 0.996) \quad (14)$$

$$T_{c0} = 529.0 \; \beta^{0.042} w_0^{0.027} \quad (r^2 = 0.995) \quad (15)$$

$$T_{c1} = 589.2 \; \beta^{0.043} w_o^{0.022} \quad (r^2 = 0.995) \quad (16)$$

where temperatures (T_m, T_{c0}, and T_{c1}) are in K, β in K/min, and w_o in mg.

The above equations manifest the close relation between the characteristic temperatures of the thermal decomposition and the procedural factors. The standardized slopes have been determined to establish the relative contribution of each independent variable and the importance of the heating rate has been assessed to be three times faster than that of the sample weight. The opposite result was found for the frequency factor where the collisions are reduced due to the "cage effect" becoming more accentuated with larger samples. It is logical to think that temperatures are more influenced by the heating rate because when the latter is increased, a higher temperature is reached for a given reaction time. Buster et al.[30] pointed out that when the heating rate increases, the maximum rate of decomposition decreases, the temperature at the maximum rate increases, and the conversion at the maximum rate increases. This article confirms part of the information reported by Bouster et al.; that is, when the heating rate increases at an approximately constant sample weight of 6.0–6.7 mg (points 1 to 5) and
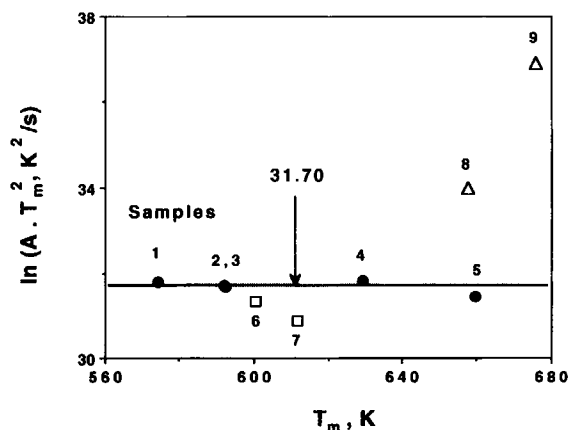

Figure 9 Compensation effect between the frequency factor and the square of temperature at the maximum decomposition rate.

25.0–25.1 mg (points 7 and 8), the temperature at the maximum rate of decomposition increases while the maximum rate of decomposition decreases. An increase of the characteristic temperatures has also been detected. However, the authors of this work have not found a significant variation of the conversion at the maximum rate of decomposition, which has approximately remained constant and equal to 0.606. Let us consider the definition of the conversion at the maximum decomposition rate from the variation of conversion with temperature:

$$f_m = \int_0^{T_m} \left(\frac{df}{dT}\right) dT \qquad (17)$$

For a first-order reaction, the value of the integral is equal to 0.6. Results found in this article confirm the theoretical value, which is constant and independent of the experimental conditions of thermal decomposition.

With respect to the influence of the variation of the sample weight at a constant heating rate, results show different trends according to the value of the heating rate. On increasing the sample weight at a constant heating rate of 1.0 K/min (points 2, 3, 6, and 7), the same situations observed for the variation of the heating rate at constant sample weight occur; that is, the temperature at the maximum decomposition rate and the characteristic temperatures increase, the maximum rate of decomposition decreases, while the conversion at the maximum decomposition rate remains constant. However, at higher heating rates (5.4–5.5 K/min for points 4 and 8, and 10.8–11.5 K/min for points 5 and 9), the same conclusions are valid except in the case of the maximum decomposition rate, which increases on increasing the sample weight. This behavior is attributable to the fact that points 8 and 9 do not provide the same activation energy as the others.

CONCLUSIONS

Dynamic thermogravimetry, with linear temperature increase, is a useful tool to study the degradation of polymeric materials, to elucidate the reaction order, and also to evaluate other kinetic parameters such as activation energy and frequency factor. Even if the overall process has no real significance with regard to the reaction mechanism, the apparent kinetic parameters (i.e., Arrhenius doublet) are useful as a means of quantifying the rate of reaction and for design purposes.

The literature mentions great variations in the activation energy of the thermal decomposition of polystyrene, taking values between 90 and 290 kJ/mol. These differences depend on several factors: (1) preparation method of the polymer (i.e., anionic, thermal, or other types of polymer preparation; lattice defects; weak links; impurities) as well as particle size; (2) Molecular weight of the polymer; (3) operating conditions (i.e., sample weight, sample particle size, heating rate, mass flow, and type of gas, thermal contact between sample, and sample holder, etc.); (4) mathematical treatment of thermogravimetric data following different computing methods (integral, differential, and special). In order to evaluate only the influence of procedural factors, such as heating rate and sample weight, it is necessary to use throughout the experimentation the same sample of polystyrene (i.e., constant molecular weight, particle size, compactness, etc.), constant air pressure, and flow rate, as well as the same computing method.

It has been found that the frequency factor decreases when sample weight and the heating rate increases. This result is supporting the hypothesis proving the importance of matrix and diffusion effects during thermal decomposition of solids. The exponent of the independent variable (either sample weight or heating rate) indicates that the frequency factor is more influenced by the sample weight than the heating rate. The reduction of the frequency factor when increasing the sample weight can be attributed to a "cage effect": the gaseous molecules formed during the thermal decomposition are trapped by the solid matrix, thus generating a recondensation/volatilization equilibrium. This effect obviously reduces the rate of decomposition, which can be related to a decrease in the frequency factor.

The activation energy is invariable (average value of $= 128.7$ kJ/mol) at low values of $\beta \cdot w_o$. In other words, when small samples are decomposed at low or moderate heating rates, the reaction mechanism remains the same and there is no mass/thermal effects as evidenced by constant activation energy values. However, when large samples are heated rapidly (i.e., high values of $\beta \cdot w_o$), the apparent activation energy increases (146–162 kJ/mol), thus indicating either a mechanism change or some problems related to heat and/or mass transfer. When a thermal decomposition takes place, the diffusion of heat and/or decomposition gases have to be considered as a simultaneous process to chemical reaction. The endothermal/exothermal reaction induces an inhomogeneous temperature distribution.

On the other hand, although constancy of heating rate in TG is generally supposed when using a linear heating program, the heating rate is perturbed in the sample when reaction is taking place. Small sample and low heating rate reduce this influence (i.e., ideal conditions).

Two characteristic temperatures (T_{c0} and T_{c1}) have been defined, which constitute the temperature interval where thermal decomposition mostly takes place. It has been demonstrated that the difference of characteristic temperatures is closely connected to the inverse of the maximum decomposition rate, whether the activation energy remains constant or not. To know whether the available data are correct, the above results prove very useful. Also, the difference of characteristic temperatures has been observed to increase on increasing the heating rate and the sample weight (only in experiments providing a constant activation energy).

Although the activation energy is usually determined from conversion and temperature data (which in general implies a great number of points to be computed for each experiment) it can also be evaluated by using: (1) temperature, conversion, and reaction rate, all of them at the maximum decomposition rate [eq. (9)]; (2) temperature and conversion at the maximum decomposition rate and characteristic temperatures [eq. (10)]; and (3) temperature at the maximum decomposition rate and characteristic temperatures [eqs. (11) and (12)]. Any of these procedures are of great interest, as they imply just one point for each experiment (just a few experiments are needed). The activation energy values found by these methods are rather similar as those obtained by the general equation [eq. (2)].

The theoretical equation demonstrating the empirical correlation proposed by Mehmet and Roche has been developed. These authors assured the existence of a linear relation between the logarithm of heating rate and the inverse of temperature at the maximum decomposition rate. In addition, this equation also allows evaluation of the activation energy by performing some experiments at variable heating rates. The activation energy evaluated in this manner is very similar to that found by the general equation [eq. (2)]. It has also been proved that there is a compensation effect between the frequency factor and the square of temperature at the maximum decomposition rate for experiments with both constant activation energy and sample weight. Therefore, an univocal relation exists between these two variables, which is of great interest as it permits the evaluation of one variable with the previous knowledge of the other.

Finally, empirical correlations relating the temperature at the maximum decomposition rate and the characteristic temperatures to the procedural factors studied in this article (i.e., heating rate and sample weight) have been obtained.

NOMENCLATURE

A:	frequency factor, s^{-1}.
df/dT:	conversion derivative or decomposition rate, K^{-1}.
$(df/dT)_m$:	maximum decomposition rate, K^{-1}.
E:	activation energy, kJ/mol.
f:	conversion.
f_m:	conversion at the maximum rate of decomposition.
R:	gas constant, 8.315 J/mol.K.
t:	time, s.
T:	temperature, K.
T_m:	temperature at the maximum rate of decomposition, K.
T_{c0}:	characteristic temperature at conversion $f = 0$, K.
T_{c1}:	characteristic temperature at conversion $f = 1$, K.
w_o:	sample weight, mg.

Greek letters

β: heating rate, K/s or K/min.

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