

A study on the thermal degradation kinetics of syndiotactic polystyrene by thermogravimetric analysis

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Abstract

The thermal degradation kinetics of syndiotactic polystyrene (sPS) has been studied by thermogravimetric analysis (TGA).

Applying both integral and differential methods, the values of the activation energy (E_a) of the degradation process during its early stages and, when possible, the Arrhenius pre-exponential factor have been determined.

All the methods appear to be suitable for the data treatment and give an E_a value of about 50 kcal mol^{-1} , compared with 60 kcal mol^{-1} for atactic PS.

INTRODUCTION

Syndiotactic polystyrene (sPS) was successfully synthesized for the first time in 1986 using catalysts based on methylaluminumoxane and titanium compounds [1–5]. Subsequently, extensive characterization has been carried out concerning its polymerization kinetics [6], and spectroscopic [7–11] and thermal properties [12–17]. Its high melting temperature (about 274°C) and very high crystallization rate led us to examine the thermal degradation phenomenon in detail because, in view of its practical use, the processing of this material will have to take place at high temperatures, well above those normally used for atactic PS.

In this preliminary study, thermogravimetric analysis (TGA) has proved to be irreplaceable: in fact, with small amounts of sample, it has allowed kinetic data on thermal degradation to be obtained in a rapid, reliable and reproducible way.

For the TGA data treatment, several methods, both differential and integral, have been reported in the literature. In this study we have used the Kissinger [18], Flynn and Wall [19] and Friedman [20] differential methods and the Van Krevelen [21], Coats and Redfern [22] and Reich

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[23,24] integral methods. All these methods gave a measure of the activation energy (E_a) and, when possible, provided the Arrhenius pre-exponential factor of the degradation reaction at an early stage, i.e. at a conversion of less than 0.25. All the values are in good agreement.

For comparison, the same treatment was performed on a thermally polymerized sample of atactic PS.

SURVEY OF METHODS FOR KINETIC ANALYSIS

The calculation methods applied in this work have been widely described [18–26]; here we give only the basic equations, referring the reader to the Experimental section and to the original papers for further details.

Kissinger's method allows the calculation of E_a from a point T_m (the maximum of the DTG curve, i.e. the conversion rate) obtained from runs at different scanning rates

$$\frac{d(\ln \beta/T_m^2)}{d(1/T_m)} = -\frac{E_a}{R} \quad (1)$$

where $\beta = dT/dt$ is the scanning rate. The activation energy can be calculated from the slope of the straight line thus obtained.

Flynn and Wall's method is used for the initial kinetic parameter measurements and is valid only at low conversions ($\alpha \ll 1$), with the assumption of $n = 0$. Taking into account the equation

$$\frac{d}{d\alpha} \left(T^2 \frac{d\alpha}{dT} \right) = \frac{E_a}{R} + 2T \quad (2)$$

E_a can be calculated from the slope of the straight line obtained by plotting the left-hand side of the above equation as a function of α .

Friedman's method has the following basic equations:

$$\ln \beta \left(\frac{d\alpha}{dT} \right) = \ln A + \ln f(\alpha) - \frac{E_a}{RT} \quad (3)$$

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

Several TGA runs at different scanning rates are needed and two subsequent plots are built with the data. The reaction rate is plotted versus $1/T$ at equal conversion; T values at constant α are taken from curves at different scanning rates. If the kinetics do not change with the conversion, one should observe a family of parallel lines having $-E_a/R$ as slope and $\ln(A(1 - \alpha)^n)$ as intercept. By plotting all these intercepts as a function of $\ln(1 - \alpha)$, a second straight line is obtained having n as slope and $\ln A$ as intercept.

Van Krevelen's method is described by the equations

$$\ln \left[\frac{(1-\alpha)^{(1-n)} - 1}{1-n} \right] = \ln \left[\frac{A}{\beta} \left(\frac{0.368}{T_m} \right)^{E_a/RT_m} \frac{1}{E_a/RT_m + 1} \right] + \left(\frac{E_a}{RT_m} + 1 \right) \ln T \quad (5)$$

for $n \neq 1$, whereas for $n = 1$

$$\ln \ln(1-\alpha) = \left(\frac{E_a}{RT_m} + 1 \right) \ln T \quad (6)$$

where T_m is the temperature at the maximum conversion rate.

Once the reaction order is chosen, the plots of the left-hand sides versus $\ln T$ give the activation energies directly. The pre-exponential factors can only be calculated for $n \neq 1$.

Reich's method also provides two different equations according to the assumed reaction order

$$\ln \ln(1-\alpha) = -\frac{E_a}{RT} + \ln \left(\frac{A\Delta T}{\beta} \right) \quad \text{for } n = 1 \quad (7)$$

$$\ln \alpha = -\frac{E_a}{RT} + \ln \left(\frac{A\Delta T}{\beta} \right) \quad \text{for } n = 0 \quad (8)$$

From the linear plots as a function of $1/T$, E_a is calculated from the slope and A from the intercept.

Coats and Redfern's method is valid assuming $n = 0$ and for $\alpha < 0.1$

$$\log \left(\frac{\alpha}{T^2} \right) = \log \frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) - \frac{E_a}{2.3R} \frac{1}{T} \quad (9)$$

The activation energy can be calculated from the slope of the straight line $\log(\alpha/T^2)$ versus $1/T$ and the pre-exponential factor can be calculated from its intercept.

All these methods, except Kissinger's and Friedman's, need a unique TGA scanning.

EXPERIMENTAL

Materials and equipment

The sample of syndiotactic polystyrene analysed was supplied by Istituto Donegani (Novara, Italy). Its weight-average molecular weight M_w measured by gel permeation chromatography in 1,2,4-trichlorobenzene at 135°C

TABLE 1

Activation energy and log of the Arrhenius pre-exponential factor for sPS and aPS

| Method | E_a (kcal mol ⁻¹) | | | | log A (min ⁻¹) | | | | |
|-------------------|---------------------------------|-----------|---------|-----------|------------------------------|-----------|---------|-----------|-----|
| | sPS | | aPS | | sPS | | aPS | | |
| | Average | Std. dev. | Average | Std. dev. | Average | Std. dev. | Average | Std. dev. | |
| Flynn and Wall | 47.7 | 2.3 | 59.4 | 1.8 | | | | | |
| Coats and Redfern | 48.9 | 2.3 | 56.7 | 2.5 | 14.7 | 0.8 | 17.2 | 0.7 | |
| Reich | | | | | | | | | |
| | $n=0$ | 51.1 | 2.1 | 58.9 | 1.5 | 16.3 | 0.7 | 18.5 | 0.7 |
| | $n=1$ | 52.3 | 2.0 | 61.2 | 2.2 | 16.8 | 0.7 | 19.3 | 0.9 |
| Van Krevelen | | | | | | | | | |
| | $n=0$ | 53.4 | 2.3 | 60.6 | 2.3 | 16.1 | 0.8 | 18.2 | 0.8 |
| | $n=1$ | 54.8 | 2.2 | 62.5 | 1.9 | | | | |
| Friedman | | 48.3 | | 35.5 | | 14.8 | | 10.2 | |
| Kissinger | | 47.4 | | 37.2 | | | | | |

(Waters 150C) was 730 000. The GPC calibration curve was obtained by using several standards of monodisperse PS.

The reference atactic PS was a thermally polymerized sample of M_w 300 000.

The thermogravimetric analyses were performed using Perkin-Elmer TGA7 equipment under nitrogen at a flow rate of 30 ml min⁻¹; before analysis, the sample (2–10 mg) was carefully purged of air. A scanning rate of 10°C min⁻¹ was generally used, except in Kissinger's and Friedman's methods, for which rates ranged from 2 to 80°C min⁻¹. Generally, the methods were applied for $\alpha < 0.25$, except for Friedman's method which was applied up to $\alpha = 0.7$.

RESULTS AND DISCUSSION

All the methods used in this work gave comparable E_a values, for both sPS and aPS. The linear regressions of the experimental data showed a correlation coefficient r^2 higher than 0.99. For sPS, E_a was about 50 kcal mol⁻¹ (Table 1).

The standard deviation of the single methods is rather small, demonstrating the considerable reproducibility of the measurements (Tables 2–6).

For aPS, the same methods gave average E_a values of around 60 kcal mol⁻¹, in very good agreement with the literature data of 61.0 kcal mol⁻¹ [26]. Only the methods of Friedman and Kissinger gave notably different results (Table 1).

The Arrhenius pre-exponential factors of sPS appear to be almost two orders of magnitude less than those for aPS (Table 1), even if a greater dispersion of data is observed (Tables 3–5). The values found for aPS are in good agreement with those reported in the literature [26].

TABLE 2

Flynn and Wall's method for sPS

| Run no. | E_a (kcal mol ⁻¹) | α_{\max} | r^2 |
|----------|---------------------------------|-----------------|--------|
| 1 | 43.3 | 0.051 | 0.9833 |
| 2 | 46.4 | 0.077 | 0.9980 |
| 3 | 48.7 | 0.053 | 0.9979 |
| 4 | 49.7 | 0.051 | 0.9995 |
| 5 | 49.7 | 0.052 | 0.9989 |
| 6 | 49.6 | 0.100 | 0.9970 |
| 7 | 46.2 | 0.051 | 0.9988 |
| Average | 47.7 | | |
| σ | 2.3 | | |

TABLE 3

Coats and Redfern's method for sPS

| Run no. | E_a (kcal mol ⁻¹) | $\log A$ | r^2 |
|----------|---------------------------------|----------|--------|
| 1 | 49.8 | 14.9 | 0.9984 |
| 2 | 46.1 | 13.7 | 0.9998 |
| 3 | 50.5 | 15.3 | 0.9990 |
| 4 | 51.0 | 15.4 | 0.9994 |
| 5 | 51.8 | 15.7 | 0.9995 |
| 6 | 47.2 | 14.2 | 0.9996 |
| 7 | 45.6 | 13.7 | 0.9993 |
| Average | 48.9 | 14.7 | |
| σ | 2.3 | 0.8 | |

TABLE 4

Reich's method for sPS

| Run no. | $n = 0$ | | | $n = 1$ | | |
|----------|------------------------------------|----------------------------------|--------|------------------------------------|----------------------------------|--------|
| | E_a (kcal mol ⁻¹) | $\log A$ (min ⁻¹) | r^2 | E_a (kcal mol ⁻¹) | $\log A$ (min ⁻¹) | r^2 |
| 1 | 50.0 | 15.9 | 0.9976 | 52.5 | 16.7 | 0.9960 |
| 2 | 48.7 | 15.5 | 0.9998 | 50.2 | 16.0 | 0.9995 |
| 3 | 52.9 | 16.9 | 0.9992 | 54.2 | 17.4 | 0.9986 |
| 4 | 53.2 | 17.0 | 0.9997 | 53.9 | 17.3 | 0.9995 |
| 5 | 54.4 | 17.4 | 0.9995 | 55.0 | 17.6 | 0.9996 |
| 6 | 49.8 | 16.0 | 0.9997 | 50.5 | 16.3 | 0.9995 |
| 7 | 48.9 | 15.7 | 0.9996 | 49.9 | 16.1 | 0.9993 |
| Average | 51.1 | 16.3 | | 52.3 | 16.8 | |
| σ | 2.1 | 0.7 | | 2.0 | 0.7 | |

TABLE 5

Van Krevelen's method for sPS

| Run no. | $n = 0$ | | | $n = 1$ | | |
|----------|------------------------------------|---------------------------------|--------|------------------------------------|---------------------------------|--------|
| | E_a (kcal mol ⁻¹) | log A (min ⁻¹) | r^2 | E_a (kcal mol ⁻¹) | log A (min ⁻¹) | r^2 |
| 1 | 51.4 | 15.4 | 0.9982 | 54.0 | | 0.9968 |
| 2 | 50.8 | 15.2 | 0.9999 | 52.2 | | 0.9998 |
| 3 | 54.9 | 16.7 | 0.9995 | 56.4 | | 0.9991 |
| 4 | 56.8 | 17.2 | 0.9994 | 58.0 | | 0.9991 |
| 5 | 55.8 | 16.9 | 0.9998 | 57.1 | | 0.9996 |
| 6 | 53.0 | 16.1 | 0.9997 | 53.8 | | 0.9998 |
| 7 | 51.0 | 15.5 | 0.9998 | 51.9 | | 0.9995 |
| Average | 53.4 | 16.1 | | 54.8 | | |
| σ | 2.3 | 0.8 | | 2.2 | | |

Table 2 summarizes the results obtained with the Flynn and Wall method, together with the maximum conversion value taken into account for the data treatment and the relative linear correlation coefficient. As can be seen, this method gives very good correlation, considering that data analysis can generally only be performed at a conversion of less than 0.05

TABLE 6

Friedman's method for sPS

| α | E_a (kcal mol ⁻¹) | r^2 |
|----------|---------------------------------|--------|
| 0.02 | 46.9 | 0.9905 |
| 0.04 | 47.0 | 0.9905 |
| 0.06 | 47.3 | 0.9933 |
| 0.08 | 48.0 | 0.9925 |
| 0.10 | 48.4 | 0.9933 |
| 0.12 | 48.3 | 0.9944 |
| 0.14 | 48.5 | 0.9927 |
| 0.16 | 48.9 | 0.9930 |
| 0.18 | 49.1 | 0.9950 |
| 0.20 | 49.1 | 0.9953 |
| 0.30 | 48.9 | 0.9948 |
| 0.40 | 48.6 | 0.9966 |
| 0.50 | 48.5 | 0.9974 |
| 0.60 | 48.1 | 0.9973 |
| 0.70 | 48.3 | 0.9957 |
| Average | 48.3 | |
| σ | 0.7 | |

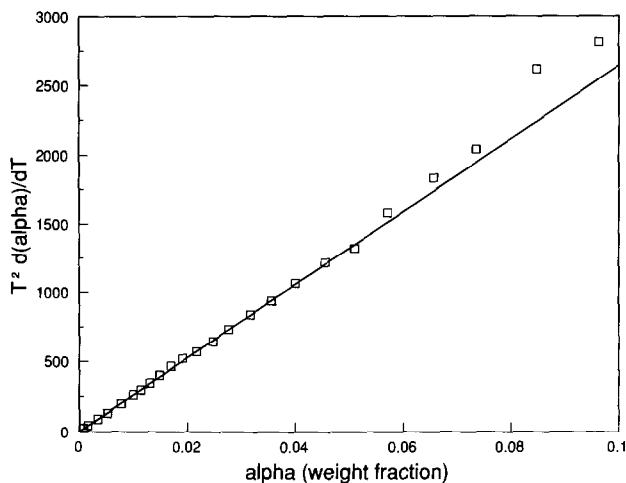


Fig. 1. Example of application of Flynn and Wall's method to sPS.

(Fig. 1), although in some cases a limit of 0.1 can be reached. Thus the assumption of zero order at very low conversions appears sufficiently valid.

Coats and Redfern's method, also valid for low conversion values ($\alpha < 0.1$), gives similar results, with very good linear correlation coefficients. Moreover, from a practical point of view, this is the most rapid method for data treatment and allows the calculation of the pre-exponential factor A (Fig. 2, Table 3).

The data handling according to the Reich method assumes either $n = 0$ or $n = 1$; in Table 4, the results are compared and, as expected [25], the E_a

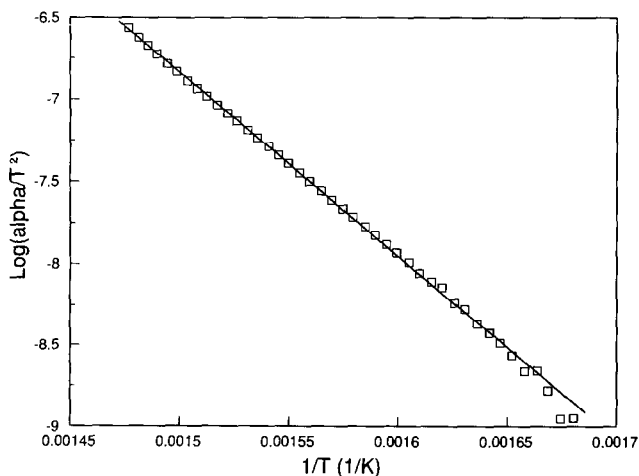


Fig. 2. Example of application of Coats and Redfern's method to sPS.

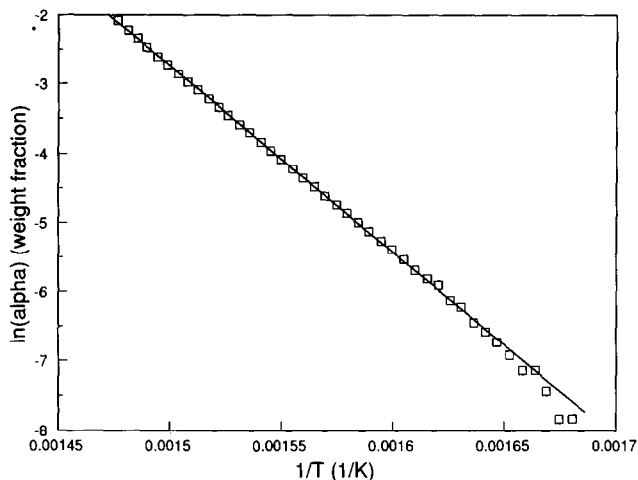


Fig. 3. Example of application of Reich's method to sPS ($n = 0$).

values for $n = 1$ are slightly higher. For $n = 0$, good agreement with the previous methods is observed (Fig. 3).

Van Krevelen's method (Table 5) gives higher activation energy values than those obtained with the other methods. This is probably due to the fact that it is necessary to go beyond the first 20–25% of conversion to determine T_m , which generally occurs at approximately 50% conversion. In fact, it has already been reported that the activation energy during the early stages of degradation is lower with respect to the subsequent reactions [22]. The introduction of T_m leads to a result that partly reflects this.

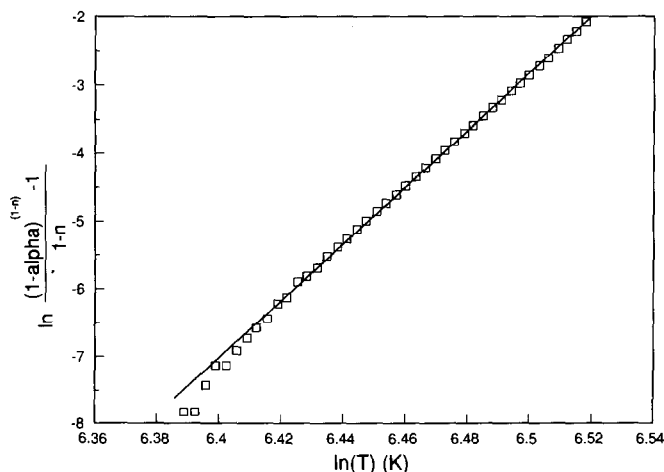


Fig. 4. Example of application of Van Krevelen's method to sPS ($n = 0$).

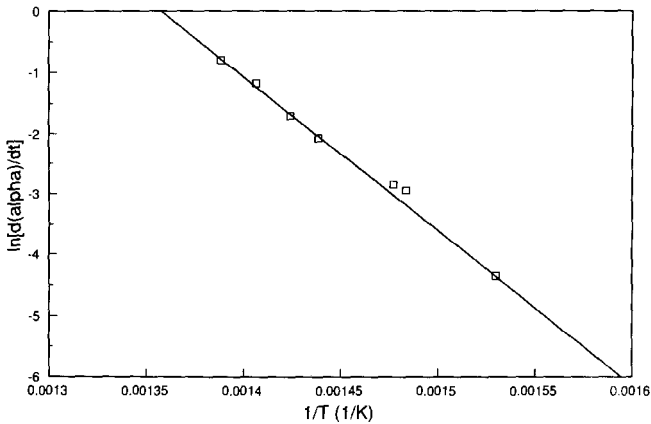


Fig. 5. Application of Friedman's method to sPS ($\alpha = 0.1$).

Even in this case we observe that the data obtained assuming $n = 1$ are slightly higher than those with $n = 0$ (Fig. 4).

Friedman's method is the most time-consuming, both because it needs several TGA runs at different scanning rates and because it provides for many linear regressions at constant α . The E_a values show a low dispersion and they are in agreement with those previously calculated (Table 6, Figs. 5 and 6). The method allows the calculation of the reaction order, which in this case was unity (Fig. 7), and of the frequency factor ($6.5 \times 10^{14} \text{ min}^{-1}$). We think, however, that the method has some limitations because small errors during the first phase of calculation can strongly influence the second phase, leading to clearly wrong values of reaction order.

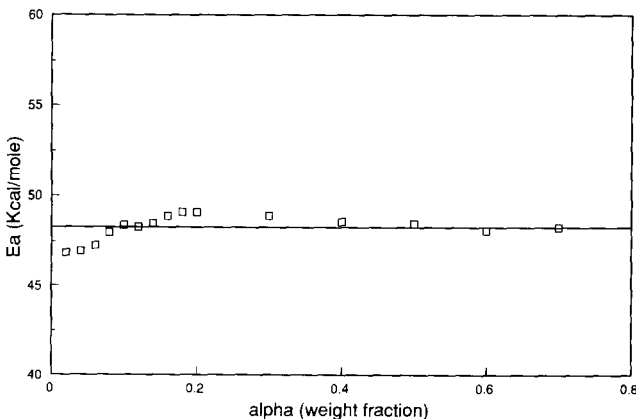


Fig. 6. Activation energy vs. α for sPS according to Friedman's method.

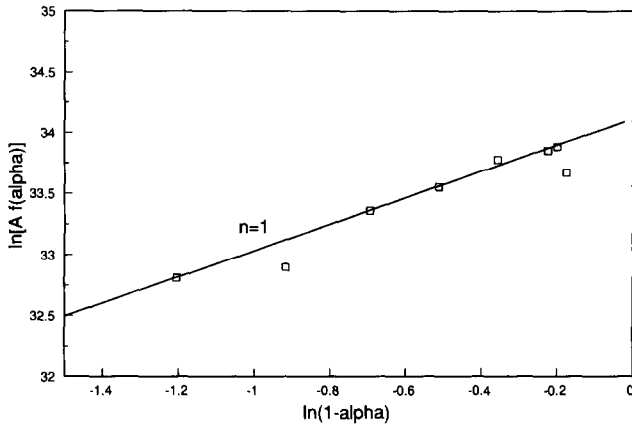


Fig. 7. Friedman's method: calculation of the reaction order for sPS ($n = 1$).

Kissinger's method seems to produce somewhat lower results than the global average (Table 1, Fig. 8). This may be because, in this case, the whole degradation curve must be taken into account and because the result derives from several runs at different scanning rates. Hence more contribution to the global error could be introduced for instrumental factors. However, the method is widely employed and has given particularly good results in the study of the oxidation of unsaturated rubbers [27,28].

The initial weight of the sample, ranging from 1 to 10 mg, does not seem to influence the final result in a significant manner.

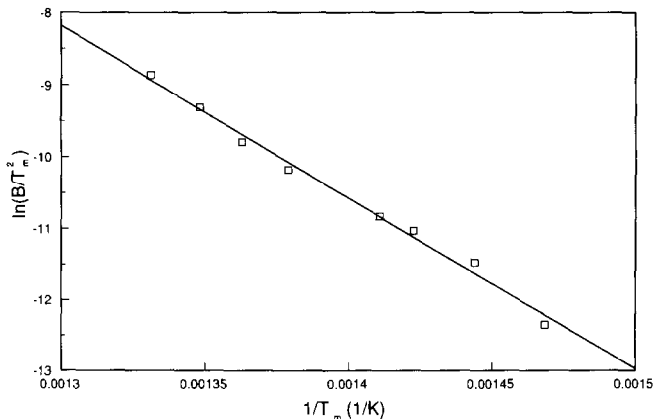


Fig. 8. Application of Kissinger's method to sPS.

CONCLUSIONS

The activation energy of the thermal degradation of syndiotactic PS with respect to atactic PS was evaluated using several methods for kinetics analysis of thermogravimetric data. The values obtained are 50 and 60 kcal mol⁻¹ respectively, with good reproducibility. When the employed method allowed it, the Arrhenius pre-exponential factor was calculated, for which a wider dispersion of values was observed.

From this set of experimental data, it can be stated that all the employed methods of kinetics analysis give reliable results and are equally applicable to the analysis of degradation kinetics data by TGA.

SYMBOLS

| | |
|------------|---|
| A | Arrhenius pre-exponential factor or frequency factor (min ⁻¹) |
| E_a | activation energy (kcal mol ⁻¹) |
| n | reaction order |
| R | universal gas constant |
| T | temperature (K) |
| ΔT | sampling interval of experimental points (K) |
| T_m | temperature of maximum reaction rate (K) |

Greek letters

| | |
|--------------|---|
| α | conversion or weight loss (weight fraction) |
| $d\alpha/dt$ | reaction rate (min ⁻¹) |
| β | TGA scanning rate (K min ⁻¹) |

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