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The value and limitations of non-isothermal kinetics in the study of polymer degradation

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Abstract

The thermal degradation of poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate) (PET) has been studied by non-isothermal thermogravimetry and a comparison made with isothermal studies. Several analytical methods have been applied to the analysis of the non-isothermal thermogravimetric (TG) data to elucidate the validity of the procedures adopted and to compare the results with isothermal procedures. In addition an alternative method of analysing the non-isothermal data is proposed, which addresses some of the shortcomings associated with the previous methods. It was found that thermal lag has a significant impact upon the calculated kinetic parameters, and extrapolation of the kinetic parameters to zero heating rate was required. It was also found that structural changes in the polymer residue during degradation brought about changes in the observed reaction order, and the kinetics of thermal degradation could only be studied to low fractional conversion.

Keywords: Thermogravimetry; Kinetics; Thermal degradation; Poly(methyl methacrylate); Poly(ethylene terephthalate)

1. Introduction

Many papers outline in detail methods for analysing non-isothermal thermogravimetric (TG) data to determine kinetic rate parameters [1–8]. Three popular methods, including those of Ozawa [1], Coats and Redfern [2] and Friedman [3] have been applied to the thermal degradation of poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate) (PET), and the differences in calculated kinetic parameters discussed, and compared with kinetic parameters derived from isothermal degradation experiments.

The degradation of PMMA was selected since the reaction is comparatively well understood and could be considered as a relatively well-behaved reaction. The major product of the decomposition is monomer and degradation is a radical depolymerisation process involving both chain end-group activated and random scission initiation of monomer elimination. The kinetics is first-order in residual sample weight and the first-order rate constants depend both on reciprocal molecular weight and the chemical composition of the end-groups [9]. The degradation of PET is less well understood but the volatile products are consistent with random chain scission and considerable molecular rearrangement of the involatile residue. The reaction kinetics are first-order in sample weight over an initial period and the first-order

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rate constant is sensitive to changes in chemical composition.

The two thermal degradation reactions—one well understood and the second open to controversy—makes them appropriate for testing the suitability of the three non-isothemal kinetic procedures to analysis polymer degradation. In addition, an alternative method of analysing non-isothermal TG data has also been proposed, and the effect of thermal lag and changes in the polymer residue during non-isothermal TG experiments investigated.

2. Experimental

PMMA used in this study was a commercial sample obtained from Elf-Atochem. It was free radically polymerised in the presence of a transfer agent, and was thought to contain predominantly saturated end-groups. PET from Dupont (Melinar) was subject to Soxhlet extraction with chloroform to remove low molecular weight oligomers. Samples were dried at 120 °C under vacuum for 24 h prior to degradation.

TG was carried out on a Stanton Redcroft STA 1000 thermobalance, with a type R thermocouple placed close to the platinum sample crucible. A flow of 40 $\text{cm}^3\,\text{min}^{-1}$ argon was passed over the sample. For non-isothermal TG, heating rates of 1.0–8.0 °C min^{-1} were chosen. Isothermal TG was carried out at temperatures between 370 and 410 °C, and the isothermal degradation temperatures were reached using a 30 °C min^{-1} heating rate.

3. The analyses of non-isothermal TG data

3.1. Ozawa method

For a simple first-order reaction Ozawa [1] derived the equation, relating the extent of conversion x to heating rate a,

$$\log f(x) \approx \log\frac{AE}{R} - \log a - 2.315 - 0.4567\frac{E}{RT} \qquad (1)$$

where $f(x)$ is a function of conversion, A is the pre-exponential factor, E is the activation energy, R is the universal gas constant and a is the heating rate. In using this equation Doyles' approximation [10,11] was adopted, i.e.

$$\frac{AE}{aR}\left[\frac{-e^y}{y} + \int_{\infty}^{y}\frac{e^y}{y}\,\mathrm{d}x\right] = \frac{AE}{aR}p(y) \qquad (2)$$

and $y = -E/RT$. When y is >20, an approximate value of $p(y)$ can be obtained using an algorithm devised by Senum and Yang [12],

$$p(y) = \frac{\exp(-x)}{x}\left(\frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}\right)$$

A plot of log a versus 1000/T at a given fractional weight should be a straight line with slope equal to $-\Delta E/R$. The activation energy is determined at 0.05 fractional weight intervals, as well as the pre-exponential factor, A, and the kinetic order of the degradation reaction.

To obtain A and the reaction order, individual plots of weight loss versus 1000/T at different heating rates are superimposed by lateral shifts, proportional to the log of the heating rate, to produce a master TG curve. This is considered to be a more accurate representation of the weight loss-temperature data and can then be compared with different forms of the thermographic curves derived for zero, first and second order degradation, or polymer degradation involving random chain scission degradation. The lateral shift required to superimpose the master curve upon the theoretical curve is equal to log A.

In particular, the theoretical weight loss-temperature curves for random degradation is,

$$\log\int\frac{\mathrm{d}x}{g(x)} = \log(-\ln(1-x)) \qquad (3)$$

where,

$$f(x) = (1-x)^{L-1}\{1 + (L-1)x\} \qquad (4)$$

for $L \ll N$, where N is the initial degree of polymerisation.

Since,

$$\log\int\frac{\mathrm{d}x}{g(x)} = \log\left(\frac{A\Delta E}{aR}\right)p\left(\frac{\Delta E}{RT}\right), \qquad (5)$$

plotting the master TG data as weight, W, versus $\log(\Delta E/aR)p(\Delta E/RT)$ produces data which can be directly compared with the theoretical master curves, shifted along the abscissa by log A. However, it must be stressed that meaningful analyses of the master TG curve cannot be performed where parallel or consecutive reactions are operating with different activation energies.

3.2. Coats and Redfern's method

This method [2] could be applied for first-order degradation processes using Eq. (6), and for other reaction orders using Eq. (7). For a first-order reaction, the extent of reaction, x, is related to temperature, T, and heating rate, a, i.e.

$$\log_{10}\left\{-\log_{10}\frac{(1-x)}{T^2}\right\} = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT} \tag{6}$$

and for reaction order, n, i.e.

$$\log_{10}\left\{\frac{1-(1-x)^{1-n}}{T^2(1-n)}\right\} = \log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT} \tag{7}$$

where T is the temperature and n the reaction order. These equations were derived using the following approximation,

$$\frac{A}{a}\int_0^T \exp^{(-E/RT)}\,\mathrm{d}T = \frac{ART^2}{aE}\left[1-\frac{2RT}{E}\right]\exp^{-E/RT} \tag{8}$$

from the mathematical approximation,

$$\int_u^\infty \exp^{-u}u^{-b}\,\mathrm{d}u \approx u^{1-b}\exp^{-u}\sum_{n=0}^{\infty}\frac{(-1)^n(b)^n}{u^{n+1}} \tag{9}$$

3.3. Friedman's method

Friedman [3] proposed that the following equation held for the non-isothermal degradation of plastics,

$$\left(\frac{-1}{w_0}\right)\left(\frac{\mathrm{d}w}{\mathrm{d}t}\right) = A\exp^{(-E/RT)}f\left(\frac{w}{w_0}\right) \tag{10}$$

where w_0 is the initial weight of material, w the weight of material at time t, A the Arrhenius pre-exponent and $f(w/w_0)$ is a function of the weight of material. Taking logs of Eq. (10) gives,

$$\ln\left(\frac{-1}{w_0}\right)\left(\frac{\mathrm{d}w}{\mathrm{d}t}\right) = \ln A + \ln f\left(\frac{w}{w_0}\right) - \frac{E}{RT} \tag{11}$$

where $f(w/w_0)$ is assumed to be constant for all values of w/w_0.

Kinetic parameters are obtained from a plot of $\ln(-1/w_0)(\mathrm{d}w/\mathrm{d}t)$ versus $1/T$ since the slope is equal to E/R and the intercept $\ln[Af(w/w_0)]$ at given values of w/w_0. Furthermore, using a value for the activation energy, the rate of weight loss and temperature an estimate of the pre-exponential factor and kinetic order can be made.

Since

$$f\left(\frac{w}{w_0}\right) = \left[\frac{(w-w_\mathrm{f})}{w_0}\right]^n \tag{12}$$

where w_f is the final weight, then,

$$\ln\left[Af\left(\frac{w}{w_0}\right)\right] = \ln A + n\ln\left[\frac{(w-w_\mathrm{f})}{w_0}\right] \tag{13}$$

The average values of ln $[Af(w/w_0)]$ obtained for each weight fraction can be plotted against $\ln[(w-w_\mathrm{f})/w_0]$, the intercept is ln A and the slope will be equal to the reaction order, n.

4. Determination of kinetic parameters from TG data

4.1. Isothermal TG measurements

First-order rate plots for the thermal degradation are shown in Fig. 1a. In both cases, deviations from linearity were observed above $x = 0.70$ and 0.5 for PMMA and PET, respectively. Only the initial linear portions of the first-order rate plots were used to calculate initial first-order rate constants. These were used in an Arrhenius plot to determine the activation energies and pre-exponential factors as shown in Fig. 1b. The activation energies were 210 ± 10 kJ mol^{-1}, and the pre-exponential factor was $(4.15 \pm 0.42) \times 10^{14}$ s^{-1} for PMMA, and 220 ± 10 kJ mol^{-1} and $(0.573 \pm 0.057) \times 10^{14}$ s^{-1} for PET.

4.2. Non-isothermal method based on Ozawa

Several non-isothermal TG curves for PMMA and PET determined at different heating rates (see Fig. 2a

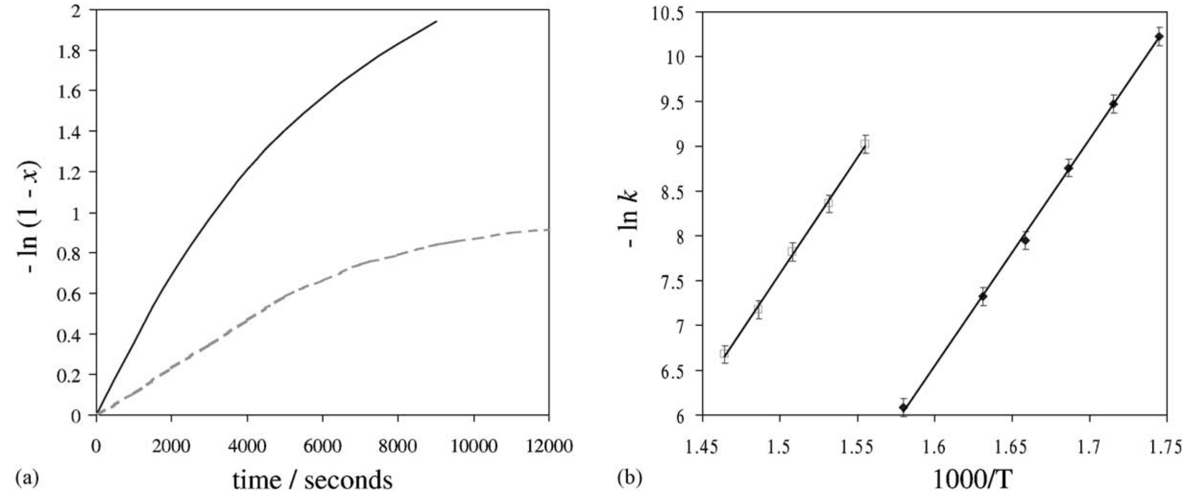

Fig. 1. Isothermal TG: (a) first-order rate plots for the thermal degradation of PMMA at 370 °C and PET at 400 °C, (- - -) PMMA, (—) PET and (b) Arrhenius plot for the thermal degradation of PMMA and PET, (◆) PMMA, (☐) PET.

and b) were used to calculate the activation energies at 0.05 fractional weight (w) intervals up to 0.95 conversion. Plots of ln$a$ versus 1000/T, see Fig. 3a and b for PMMA and PET, respectively were linear but the activation energies varied with w, as can be seen in Fig. 4 but the average activation energies for PMMA and PET were 210 ± 10 and 180 ± 10 kJ mol^{-1}, respectively in excellent agreement with that calculated for PMMA from isothermal data (210 ± 10 kJ mol^{-1}), but not in the case of PET where there was a discrepancy of 40 kJ mol^{-1}. This difference may reflect the analyses being extended to higher conversions than those used in the isothermal rate analyses.

It has been claimed that the pre-exponential factor can be determined from non-isothermal data by superimposing experimental TG data obtained at different heating rates on to a theoretical plot for the kinetic order determined. The lateral shifts determine the pre-exponential factor. Master curves for PMMA and PET were produced by shifting each TG curve on to that of the lowest heating rate, and averaging the temperature

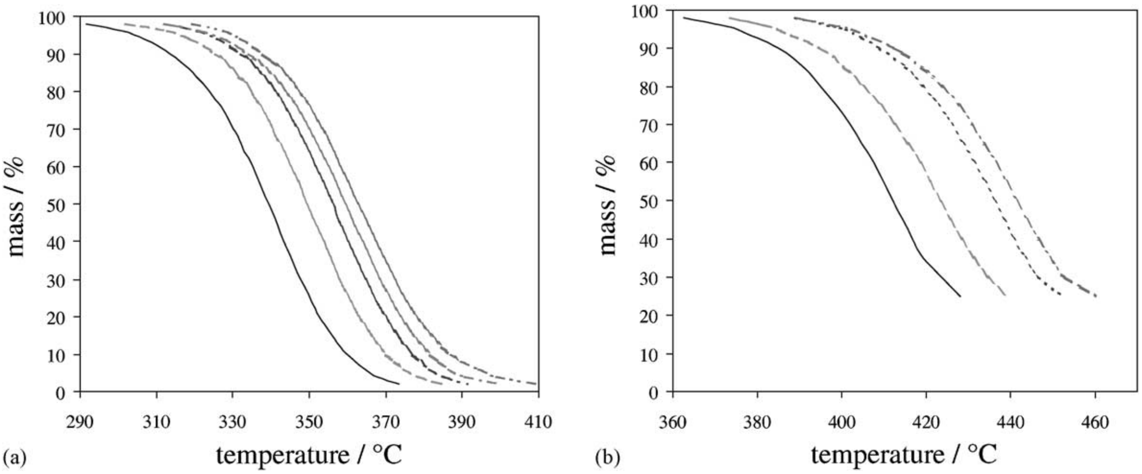

Fig. 2. Non-isothermal TG: (a) PMMA and (b) PET.

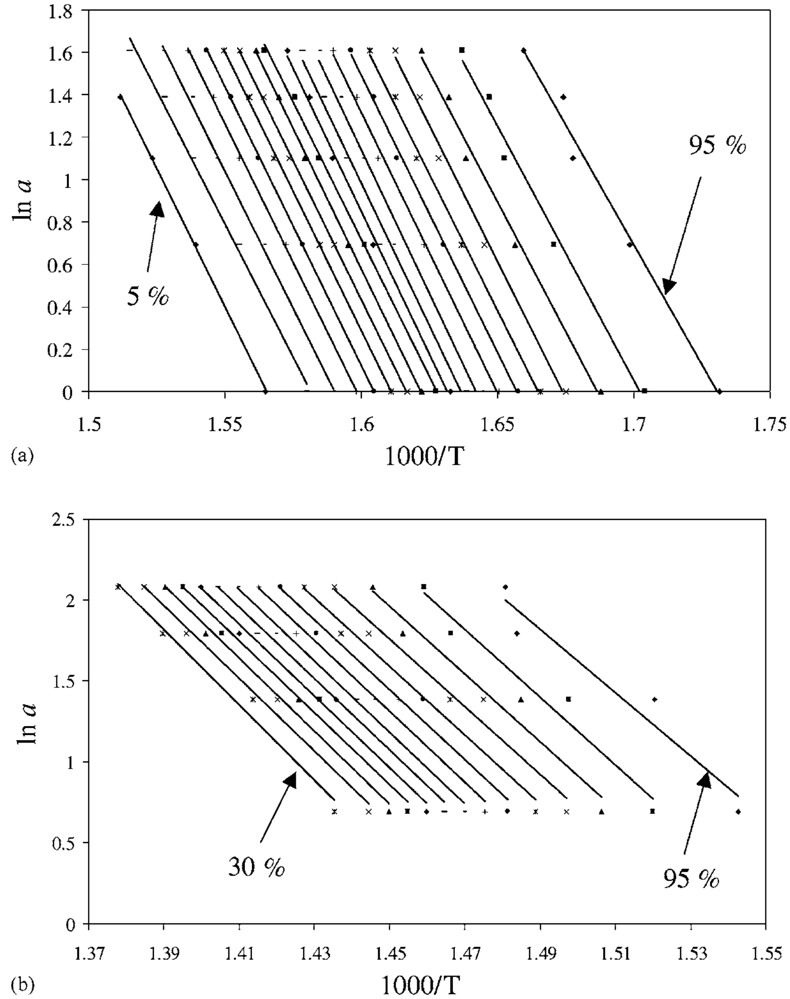

Fig. 3. Determination of activation energy by Ozawa's method: (a) PMMA and (b) PET.

for each value of W. The master curves for PMMA and PET are shown in Fig. 5, and replotted as W versus $\log\{(\Delta E/aR)p(\Delta E/RT)\}$, see Fig. 6. The plots were then fitted to theoretical plots, and the lateral shift required to superimpose the master TG data onto the theoretical data was equal to $\log A$, where A is the pre-exponential factor. It was found that the master TG data from PMMA fitted a first-order curve acceptably (see Fig. 7). The lateral shift gave a pre-exponential factor of $(8.91 \pm 0.89) \times 10^{14}\ \mathrm{s}^{-1}$, about double that determined from isothermal data, $(4.15 \pm 0.42) \times 10^{14}\ \mathrm{s}^{-1}$, although the natural log of these values, 34.42 and 33.66 respectively, show the results to be similar.

The analogous procedure for PET is shown in Fig. 8. The non-isothermal data could not be fitted to a first-order weight dependence, nor could it be fitted the random scission plots with any degree of precision. The pre-exponential factor for PET was consequently found to be $(6.310 \pm 0.063) \times 10^{10}\ \mathrm{s}^{-1}$, compared to $(0.573 \pm 0.057) \times 10^{14}\ \mathrm{s}^{-1}$ calculated from isothermal data.

4.3. Coats and Redfern's non-isothermal method

The activation energy for the thermal degradation of PET was determined assuming first-order kinetics from a plot of $\log_{10}\{-\log_{10}((1-x)/T^2)\}$ versus $1/T$

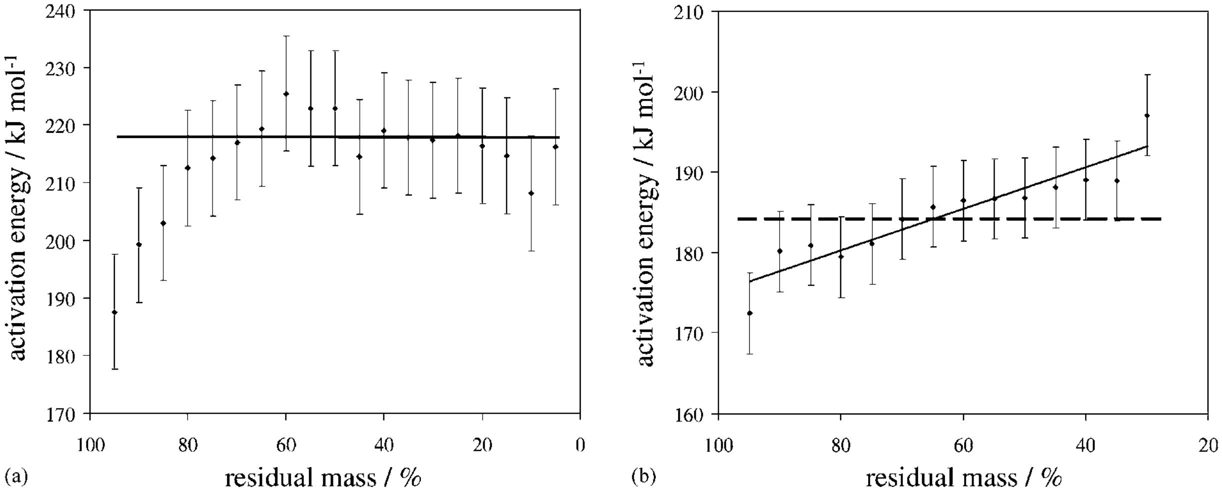

Fig. 4. Variation in activation energy with residual weight determined by Ozawa's method: (a) PMMA and (b) PET.

as shown in Fig. 9. The activation energy was calculated from the initial linear portions of the weight loss against temperature from $x = 0.05$ to 0.30. The linearity of the plots and the activation energies varied with heating rate (see Fig. 10). Although, there was considerable scatter the activation energy for PMMA on extrapolation to zero heating rate, was 210 ± 20 kJ mol^{-1}, which was in excellent with that determined from isothermal data (210 kJ mol^{-1}). The activation energies calculated for PET showed more scattering, but did not exhibit a trend with heating rate. The values varied between 250–290 kJ mol^{-1}. The Coats and Redfern's method could not be used to calculate the pre-exponential factor.

4.4. Friedman's non-isothermal method

The Friedman's method [3] was used to deduce the activation energy, pre-exponential factor and reaction order for the thermal degradation of PMMA and PET. The activation energies were calculated at 0.05 fractional weight intervals, by plotting

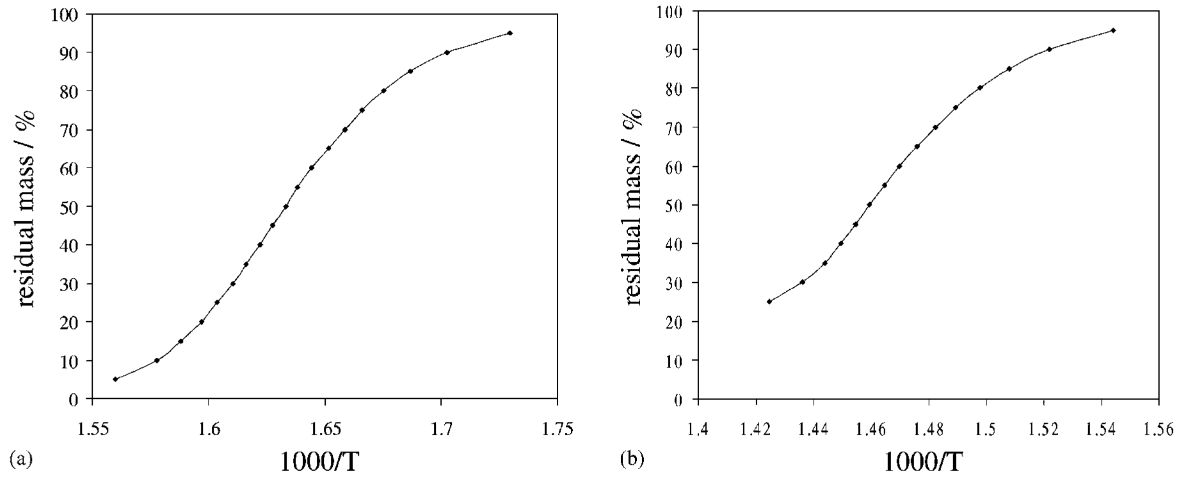

Fig. 5. Master TG curve for: (a) PMMA and (b) PET.

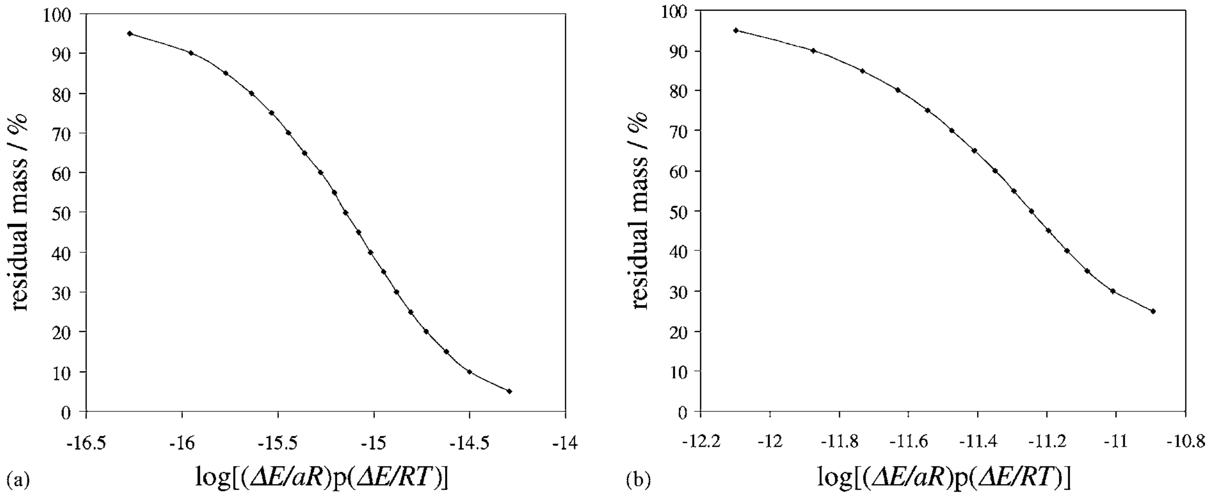

Fig. 6. Master TG data converted for comparison to theoretical curves: (a) PMMA and (b) PET.

$-\ln\,[(-1/w_0)(\mathrm{d}w/\mathrm{d}t)]$ against 1000/T, where w is residual weight, t the time, w_0 the initial weight and T the temperature. These plots for PMMA and PET are shown in Fig. 11, and the variation in kinetic parameters with fractional weight are shown in Figs. 12 and 13. The activation energies were found to vary with residual weight, but this was compensated in each case by a variation in the value of the intercept, $\ln\,[A\,f\,(w/w_0)]$, as shown by Friedman [3]. The average activation energy for the thermal degradation of PMMA was again $210 \pm 10\,\mathrm{kJ\,mol^{-1}}$, in agreement with that obtained from isothermal data. In the case of PET, the activation energy was found to be $170 \pm 10\,\mathrm{kJ\,mol^{-1}}$, which was considerably

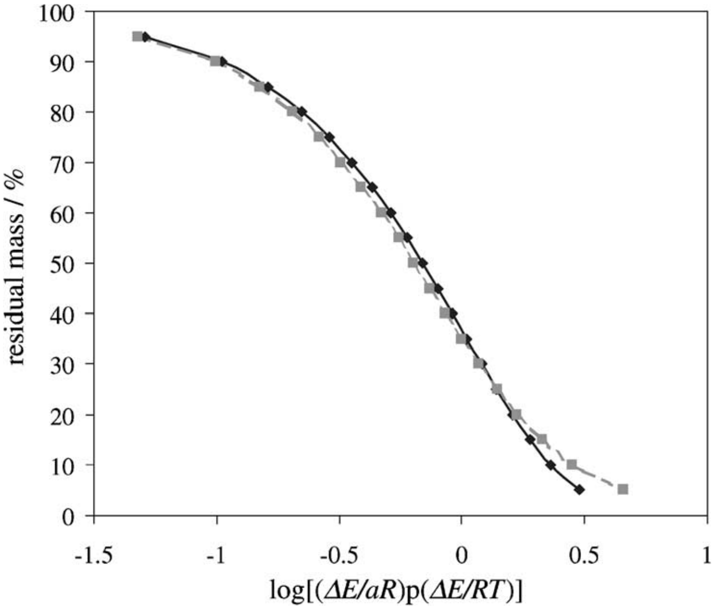

Fig. 7. Master TG curve for PMMA superimposed on theoretical first-order (■) curve and (◆) theoretical first-order.

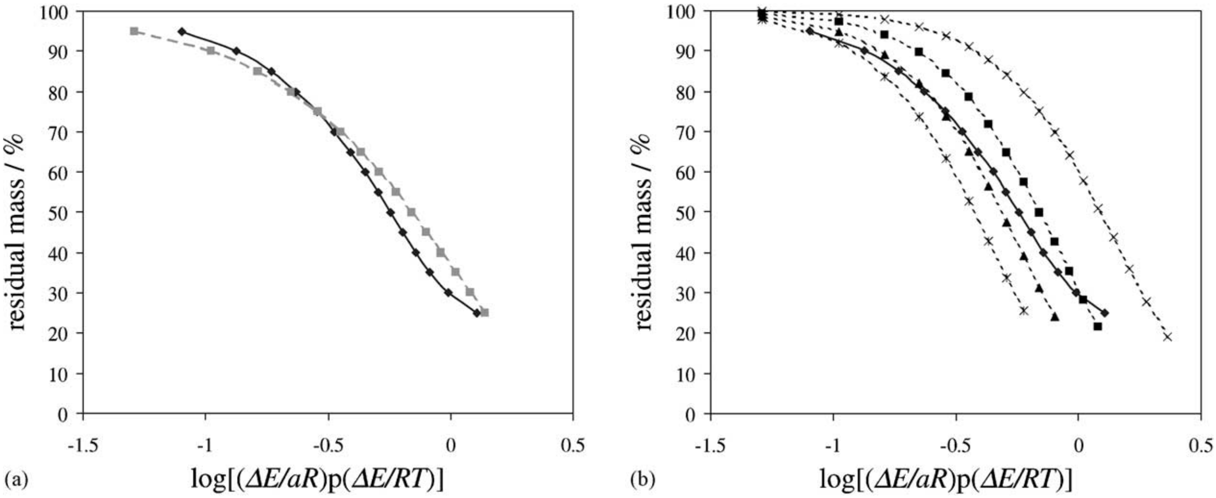

Fig. 8. Master TG data for PET superimposed on, (a) theoretical first-order curve: (■) theoretical first-order, (◆) PET and (b) theoretical random scission: (×) $L = 2$, (▲) $L = 3$, (■) $L = 4$ and (⋇) $L = 5$.

lower than that determined from isothermal TG data, 220 ± 10 kJ mol^{-1}.

In addition the pre-exponential factor and the kinetic order were determined using Eq. (14) and the average activation energy, ΔE, i.e.

$$\ln\left[\left(\frac{(-1)}{w_0}\right)\left(\frac{\mathrm{d}w}{\mathrm{d}t}\right)\right] - \frac{\Delta E}{R} = \ln A + \ln\left[f\left(\frac{w}{w_0}\right)\right] \quad (14)$$

w_f (see Eq. (12)) was used to account for the weight of involatile residue at the end of the decomposition. ln A and the reaction order was obtained from the intercept and slope, respectively. w_f was found to be approximately 0.02 and 0.18 for PMMA and PET respectively, The pre-exponential factors and kinetic orders for PMMA and PET are shown in Fig. 14. In both cases the plots were non-linear.

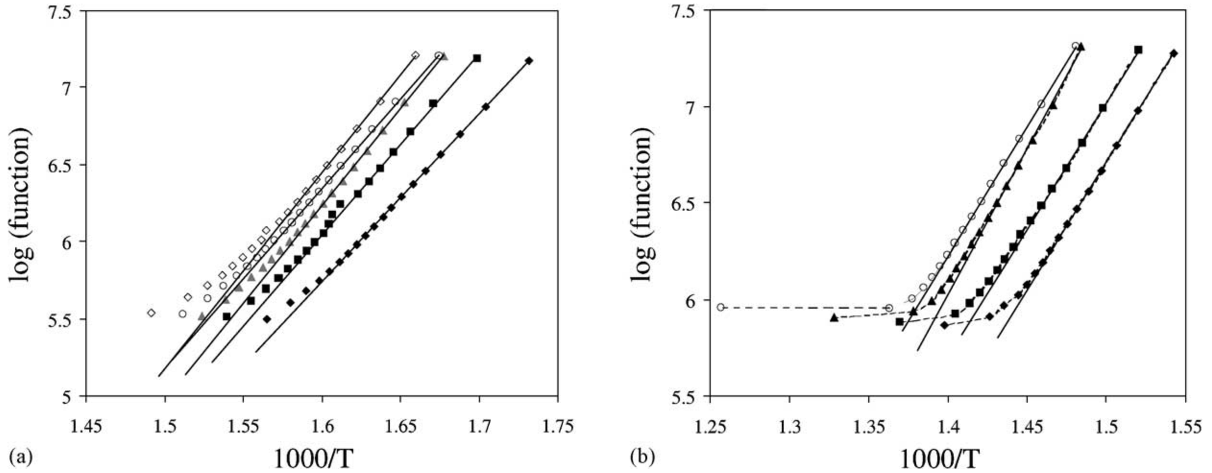

Fig. 9. Determination of activation energy by Coats and Redfern's method, (a) PMMA: (◆) 1 °C min^{-1}, (■) 2 °C min^{-1}, (▲) 3 °C min^{-1}, (○) 4 °C min^{-1}, (◇) 5 °C min^{-1} and (b) PET: (◆) 1 °C min^{-1}, (■) 2 °C min^{-1}, (▲) 3 °C min^{-1}, (○) 4 °C min^{-1}, (◇) 5 °C min^{-1}.

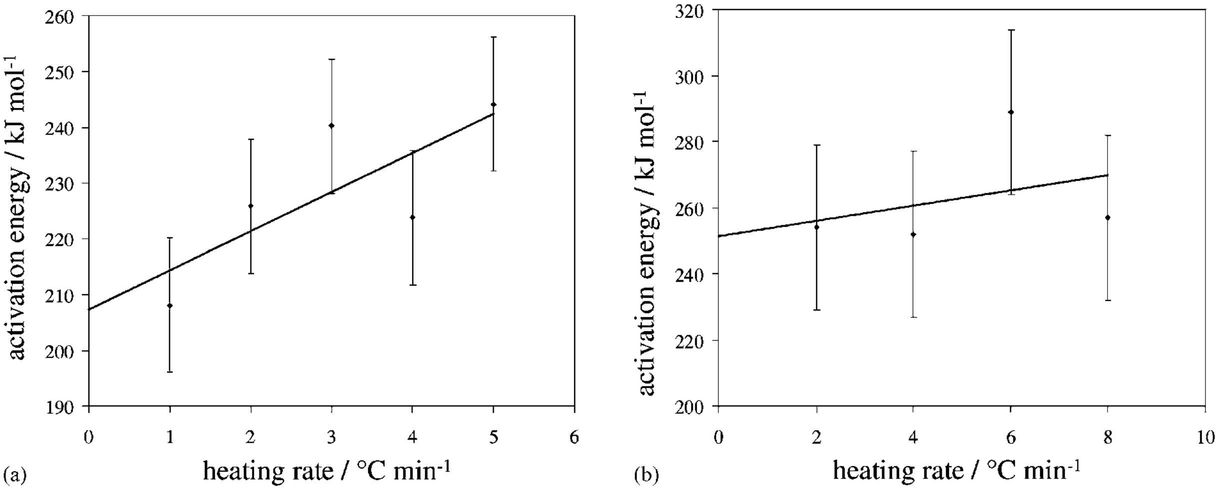

Fig. 10. Variation in activation energy with heating rate calculated by Coats and Redfern's method: (a) PMMA and (b) PET.

5. An alternative approach to analysing non-isothermal TG data

5.1. First-order kinetics

An alternative approach to interpreting non-isothermal data for polymer degradation was derived initially assuming first-order kinetics, although other orders could be assumed and the data analysed from the appropriate integrated rate equation (see Table 1). From the weight loss versus temperature data, the fractional conversion was calculated at 0.005 intervals. Assuming first-order kinetics, $-\ln(1-x)$ was plotted against time, t i.e.

$$-\ln(1-x) = kt \tag{15}$$

Differentiating with time gives the rate constant, k, as a function of conversion and also time, i.e.

$$\frac{-\mathrm{d}[\ln(1-x)]}{\mathrm{d}t} = \frac{\mathrm{d}kt}{\mathrm{d}t} = k \tag{16}$$

Table 1
Integrated rate equation for different reaction orders

Reaction order	Integrated rate equation
Zero	$x = kt$
First	$-\ln(1-x) = kt$
Second	$\frac{1}{x} - 1 = kt$
Third	$\frac{1}{x^2} - 1 = kt$

Converted the time axis to temperature, T, from the known heating rate enable an Arrhenius plot of $-\ln\{\mathrm{d}[-\ln(1-x)]/\mathrm{d}t\}$ versus $1000/T$ to be made. The slope is E/R and an intercept $\ln A$.

Finally, to eliminate thermal lag effects E and $\ln A$ as calculated at several heating rates were linearly extrapolated to zero heating rate.

5.2. Determination of reaction order

In situations where the order of the degradation process was not known, it was possible to determine the order. At any temperature, the rate of loss of material, $\mathrm{d}x/\mathrm{d}t$, is,

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = kx^n \tag{17}$$

where x is the fractional weight, t the time, k the reaction rate constant and n the order of reaction. Using the Arrhenius relationship,

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = A\exp^{(-E/RT)}x^n \tag{18}$$

from which

$$-\ln\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) = \ln A + n\ln x - \frac{E}{RT} \tag{19}$$

E/R can be estimated from a plot of $\ln(\mathrm{d}x/\mathrm{d}t)$ versus $1000/T$ at low conversion, and slow heating rate ($<2\ \mathrm{K\ min}^{-1}$). Since $\ln A$ in Eq. (19) is constant, it can

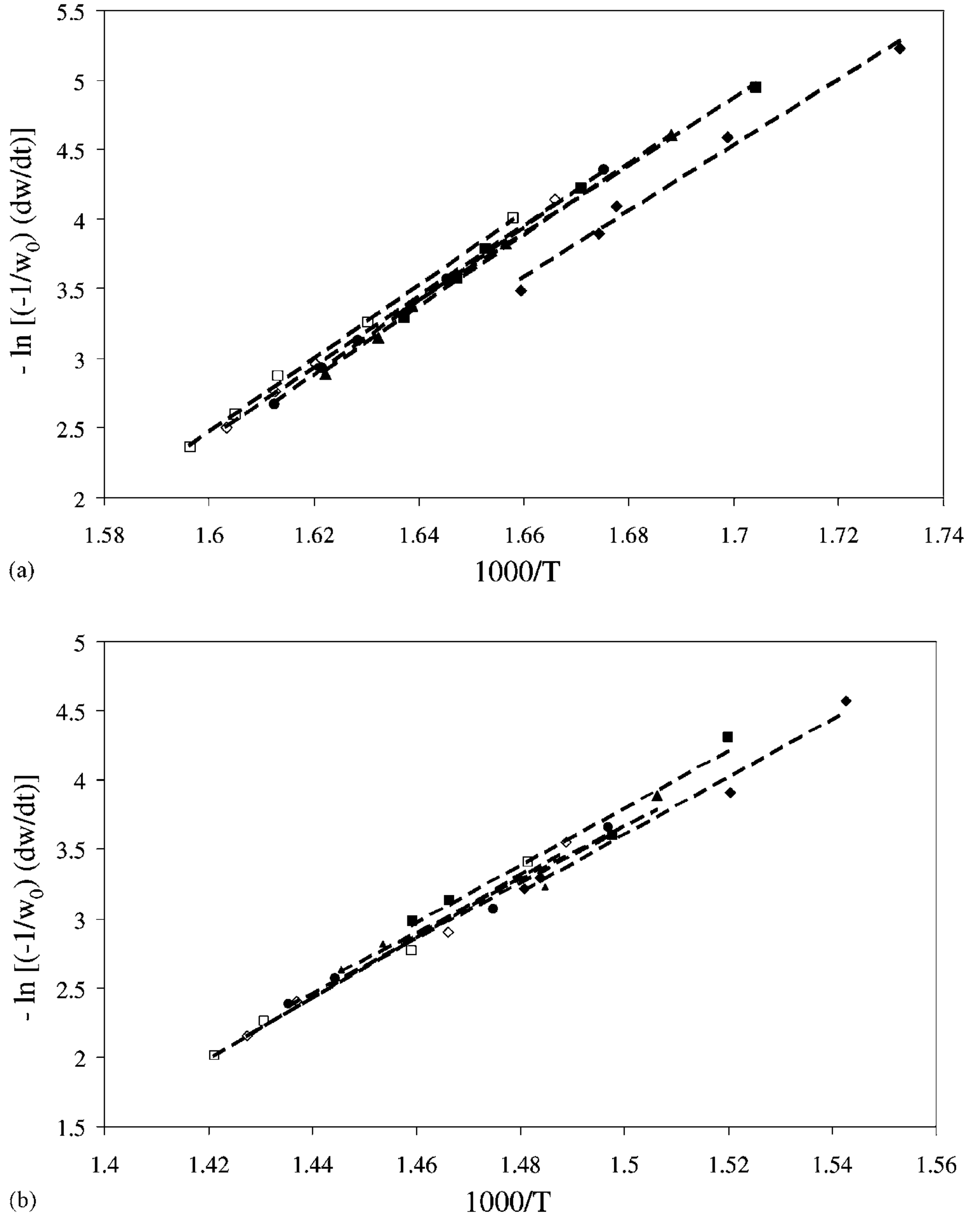

Fig. 11. Determination of activation energy using the Friedman's method, (a) PMMA: (◆) 95%, (■) 90%, (▲) 85%, (●) 80%, (◇) 75%, (□) 70% and (b) PET: (◆) 95%, (■) 90%, (▲) 85%, (●) 80%, (◇) 75%, (□) 70%.

be eliminated, i.e.

$$\ln\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_1 - n\ln x_1 + \frac{E}{RT_1} = \ln\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_2 - n\ln x_2 + \frac{E}{RT_2} \quad (20)$$

for which

$$n\ln x_2 - n\ln x_1 = \ln\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_2 - \ln\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_1 + \frac{E}{RT_2} - \frac{E}{RT_1} \quad (21)$$

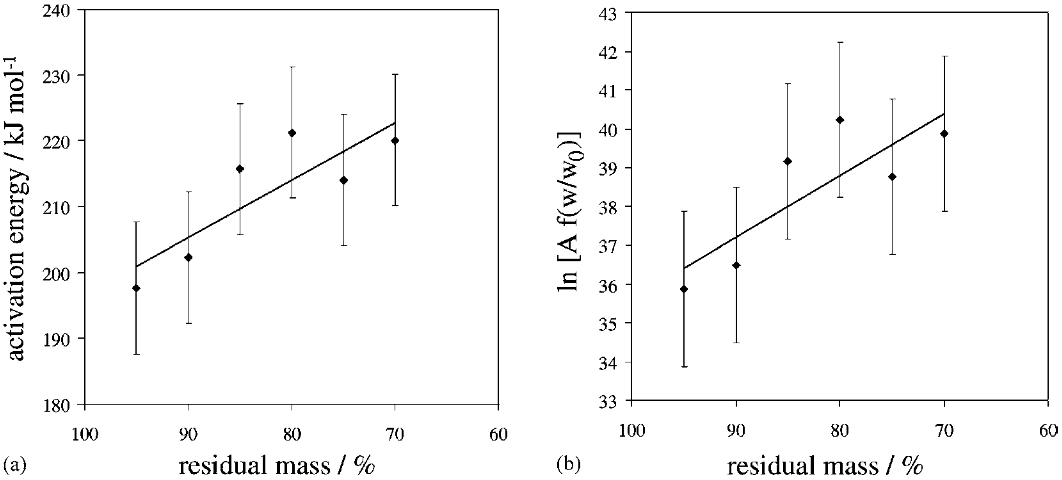

Fig. 12. Variation in kinetic parameters for the thermal degradation of PMMA: (a) activation energy and (b) ln $[A\,f\,(w/w_0)]$.

If isokinetic points are chosen on either side of the maximum of a differential TG curve, the rate terms in Eq. (21) can be eliminated, and the corresponding values of x and T associated with the isokinetic points can be used to calculate the reaction order, n, from

$$n = \frac{(E/RT_2 - E/RT_1)}{\ln x_2 - \ln x_1} \tag{22}$$

Alternatively, if it is necessary to calculate n over a short initial period (e.g. the first 10% conversion), due to changes in reaction order in the later stages of the degradation, n can be calculated from

$$n = \frac{\ln(\mathrm{d}x/\mathrm{d}t)_2 - \ln(\mathrm{d}x/\mathrm{d}t)_1 + (E/RT_2 - E/RT_1)}{\ln x_2 - \ln x_1} \tag{23}$$

which can be reduced to,

$$n = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]\left[\ln\frac{x_1}{x_2}\right] \tag{24}$$

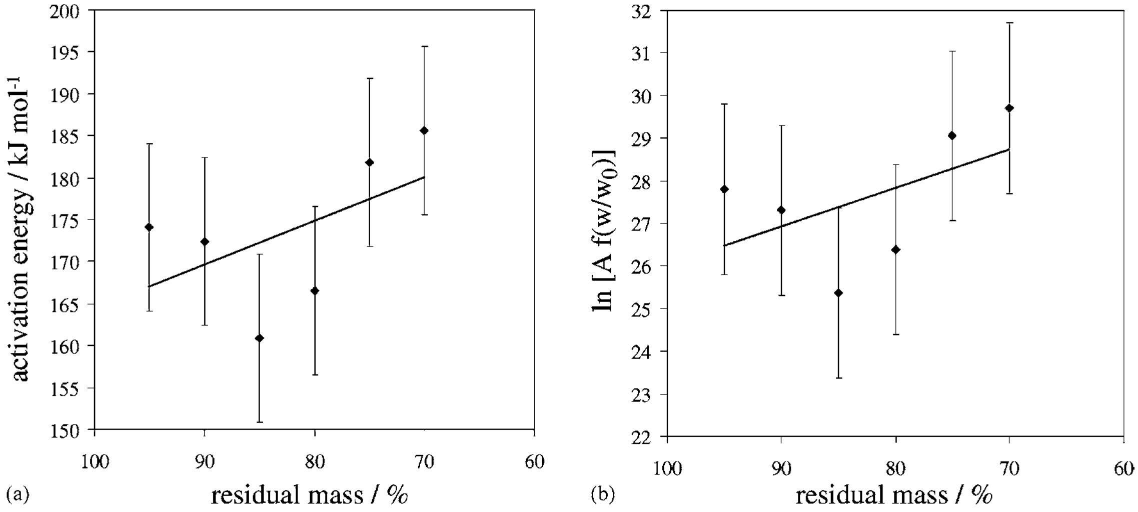

Fig. 13. Variation in kinetic parameters for the thermal degradation of PET: (a) activation energy and (b) ln $[A\,f\,(w/w_0)]$.

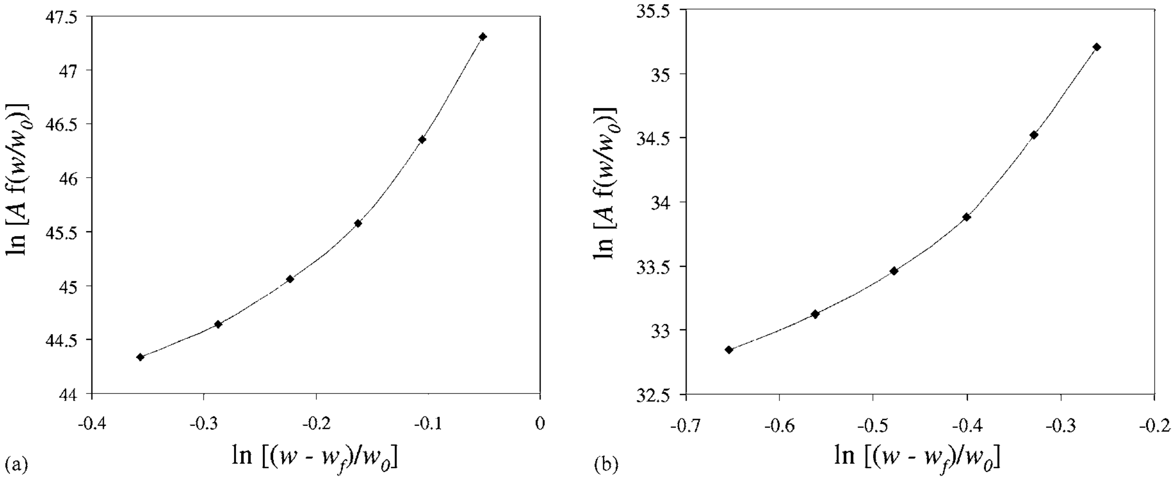

Fig. 14. Determination of the pre-exponential factor by the Friedman's method: (a) PMMA and (b) PET.

Once *n* has been determined, the appropriate rate equation can be applied to the method described in Section 5.1. This procedure is more likely to provide a closed estimate of the value of *E*, which in turn can be used to calculate *A*.

5.3. Application to the degradation of PMMA and PET

In the thermal degradation of polymers, weight loss is generally observed to be first-order in residual weight over an initial period. However, deviations are observed at high conversions, due to side reactions (e.g. formation of cross-links or side-group elimination) or changes to the sample such as reduction in molecular weight, end-group concentration etc. To avoid possible problems associated with deviations from first-order kinetics, the first 0.10 fractional weight loss only was analysed.

The temperature corresponding to 0.005 fractional weight loss intervals were determined and plotted against time. This was differentiated to produce plots of the apparent rate constant, *k*, versus time. This process is illustrated for PMMA heated at 1 K min^{-1} in Fig. 15. The activation energy and the pre-exponential factor, at each heating rate, were subsequently determined from Arrhenius plots. These plots for the thermal degradation of PMMA at five heating rates are shown in Fig. 16. The plot of activation energy versus heating rate was extrapolated to zero heating rate in Fig. 17a and the activation energy found to be 200 ± 10 kJ mol^{-1}, compared to 210 ± 10 kJ mol^{-1} obtained from the isothermal data. Similarly, a plot of ln *A* versus heating rate extrapolated to zero heating rate (Fig. 17b) gave a pre-exponential factor of $(2.26 \pm 0.11) \times 10^{14}\ \text{s}^{-1}$ compared to $(4.15 \pm 0.42) \times 10^{14}\ \text{s}^{-1}$ from isothermal experiments, in good agreement.

The non-isothermal TG data of PET was subject to the same analyses, and the Arrhenius plots showing the results of degradation at four heating rates are shown in Fig. 18. A plot of activation energy versus heating rate was linear, see Fig. 19a and b, but with considerable scatter. The extrapolated value, to zero heating rate, for the activation energy of 220 ± 10 kJ mol^{-1} was identical to that obtained from the isothermal experiments. Similarly, a plot of ln *A* versus heating rate, Fig. 19c also exhibited considerable scatter but the pre-exponential factor extrapolated to zero heating rate was found to be $(8.63 \pm 0.43) \times 10^{13}\ \text{s}^{-1}$close to that obtained from the isothermal experiments, i.e. $(5.73 \pm 0.57) \times 10^{13}\ \text{s}^{-1}$.

5.4. Reaction order determinations

To test the validity of this method, it was applied to non-isothermal TG data from PMMA and PET. The first step involved estimating the activation energy of

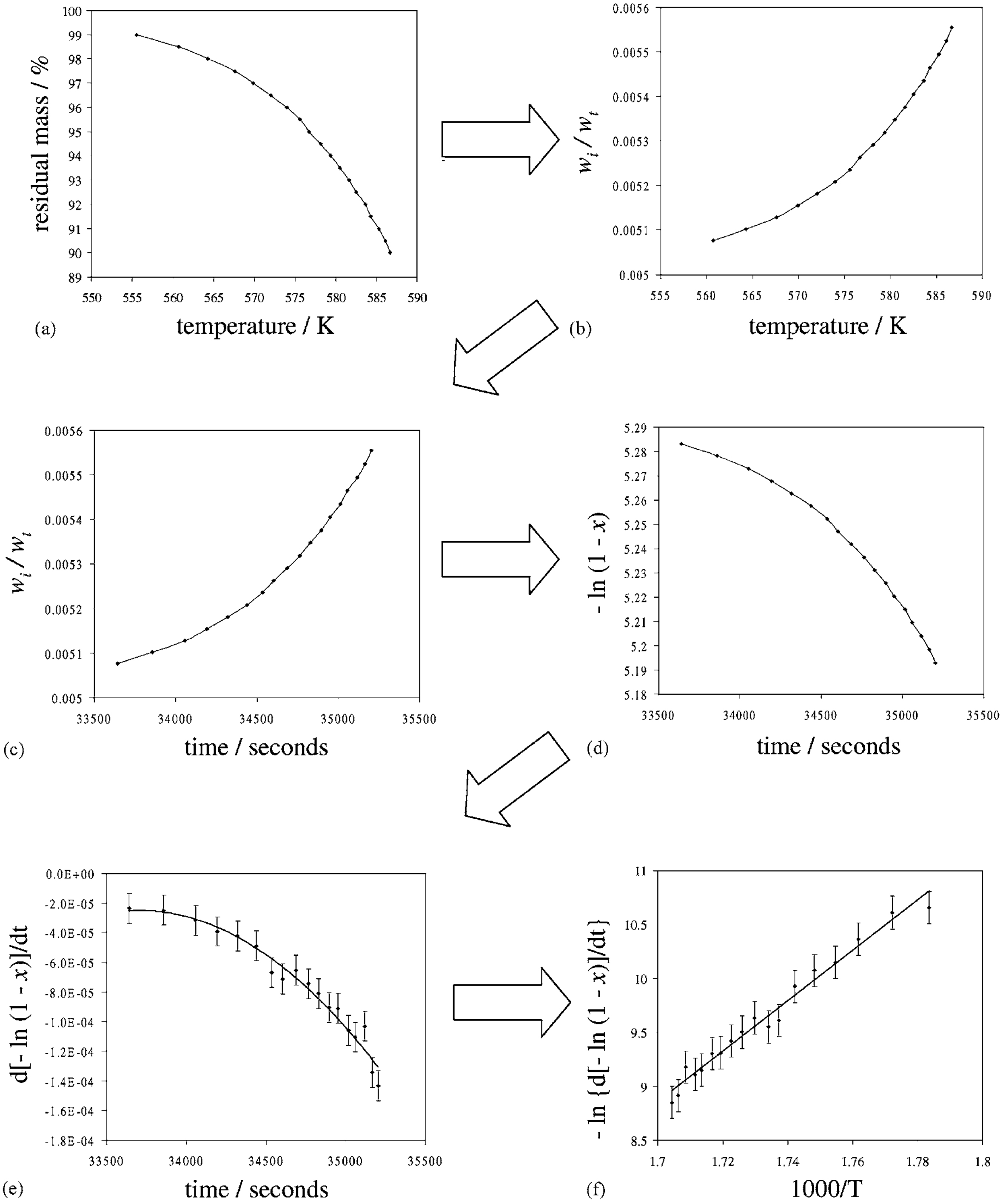

Fig. 15. Demonstration of alternative method of analyses of non-isothermal data for PMMA at 1 °C min^{-1}.

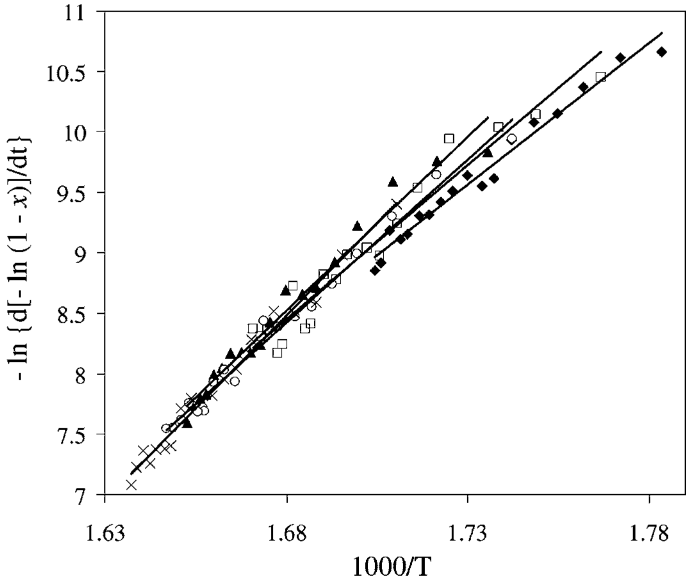

Fig. 16. Determination of kinetic parameters for the thermal degradation of PMMA at different heating rates: (◆) 1 °C min^{-1}, (▲) 2 °C min^{-1}, (□) 3 °C min^{-1}, (○) 4 °C min^{-1}, and (×) 5 °C min^{-1}.

the weight loss process. This was carried out from a plot of ln (dx/dt) versus 1000/T, where x is residual weight, t the time and T the temperature. For PMMA, the activation energy was initially estimated, as being 190 ± 10 kJ mol^{-1}, from the weight–temperature data obtained at the slowest heating rate, 1.0 K min^{-1}, see Fig. 20. This value was lower than that determined by other methods, i.e. 210 ± 10 kJ mol^{-1} and implies that the $n\ln x$ term in Eq. (19) cannot be treated as unimportant. Isokinetic points were chosen from the differential TG curve, see Fig. 21a, and the corresponding temperatures, T_1 and T_2, and fractional weights determined from Fig. 21b. The reaction order, n, was found to be 1.1 ± 0.1 consistent with the

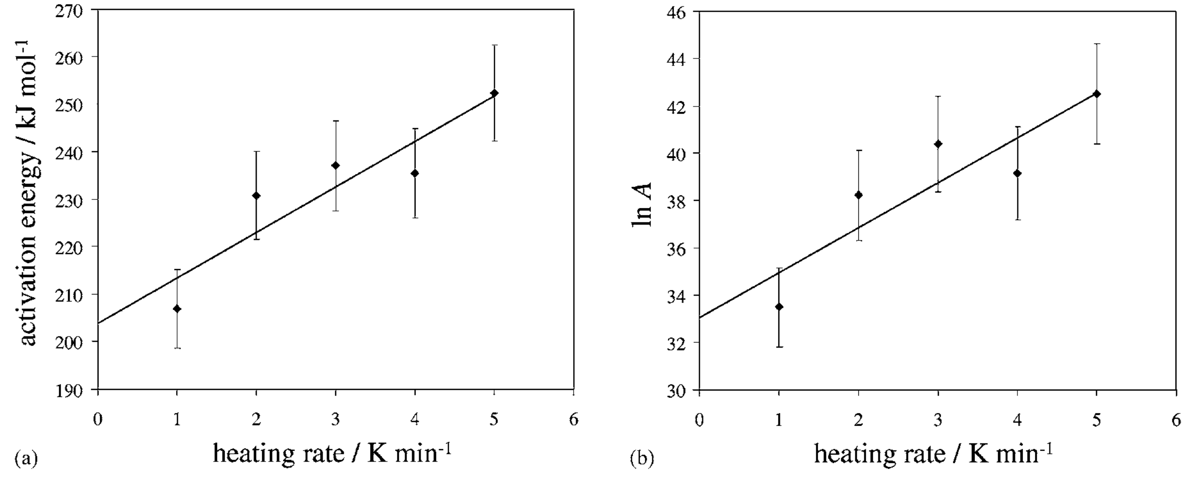

Fig. 17. Variation of kinetic parameters with heating rate for PMMA: (a) activation energy and (b) pre-exponential factor.

degradation of PMMA being first-order in weight loss.

This analyses was carried out on PET, see Fig. 22, but this time at a heating rate of 2 K min^{-1}. The activation energy was found to be 220 ± 10 kJ mol^{-1}, and the reaction order was 1.5 ± 0.1 and not 1.0 as determined above by isothermal experiments.

The analyses was repeated, on both PMMA and PET, but restricted to 0.10 fractional weight intervals. Plots of reaction order against residual weight are shown in Fig. 23. Within experimental error, the reaction order of PMMA remained constant with conversion, and the average reaction order was 1.14 ± 0.12. However, with PET the reaction order was constant at 1.01 ± 0.18 within experimental error only over an initial 0.40 weight fraction. Above this, the reaction order rose steeply with conversion.

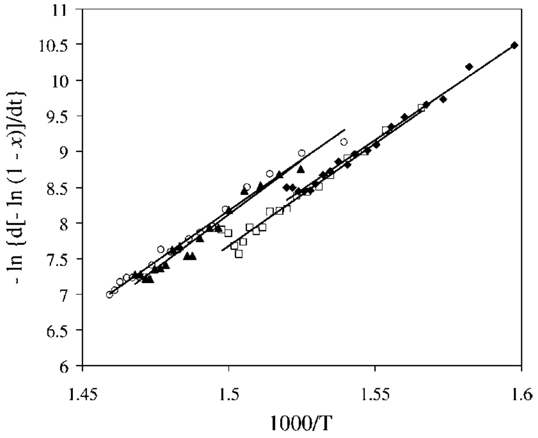

Fig. 18. Determination of kinetic parameters for the thermal degradation of PET at different heating rates: (◆) 2 °C min^{-1}, (□) 4 °C min^{-1}, (▲) 6 °C min^{-1}, (○) 8 °C min^{-1}.

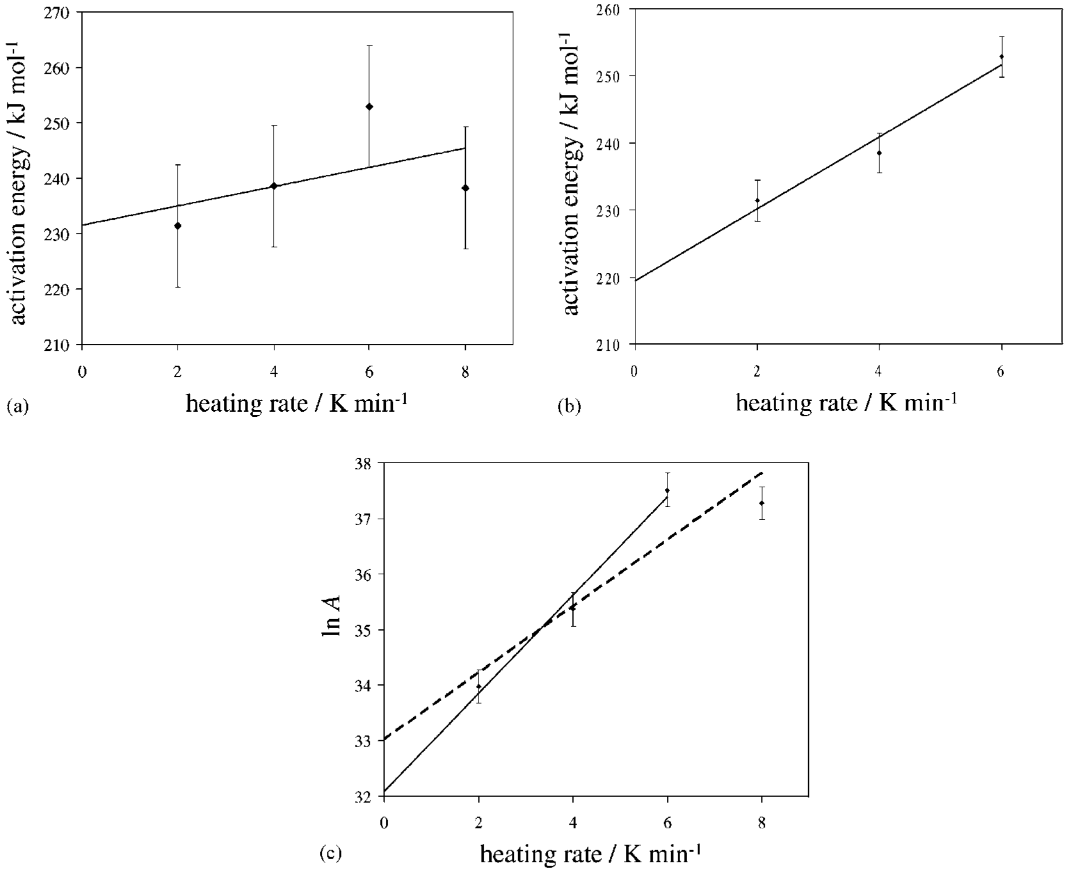

Fig. 19. Variation of kinetic parameters with heating rate for PET: (a) activation energy (b) activation energy excluding result at 8 °C min^{-1}, and (c) pre-exponential factor.

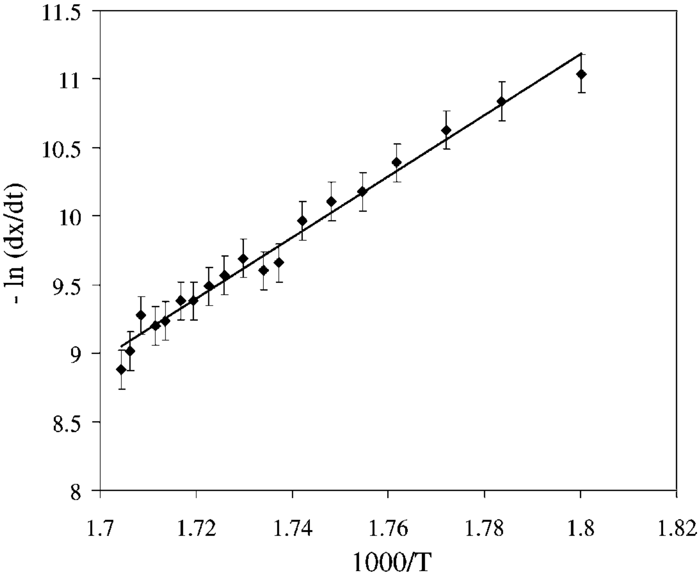

Fig. 20. Determination of kinetic parameters for PMMA at 1 °C min^{-1} to determine reaction order.

6. The effect of heating rate and thermal lag on non-isothermal thermogravimetry

It was apparent that some of the differences between the changes in kinetic parameters of the thermal degradation at different heating rates were due to thermal lag across the specimen. To investigate this effect, a model for non-isothermal degradation was produced for comparison with the experimental non-isothermal data. The first-order integrated weight equation is,

$$-\ln w = kt$$

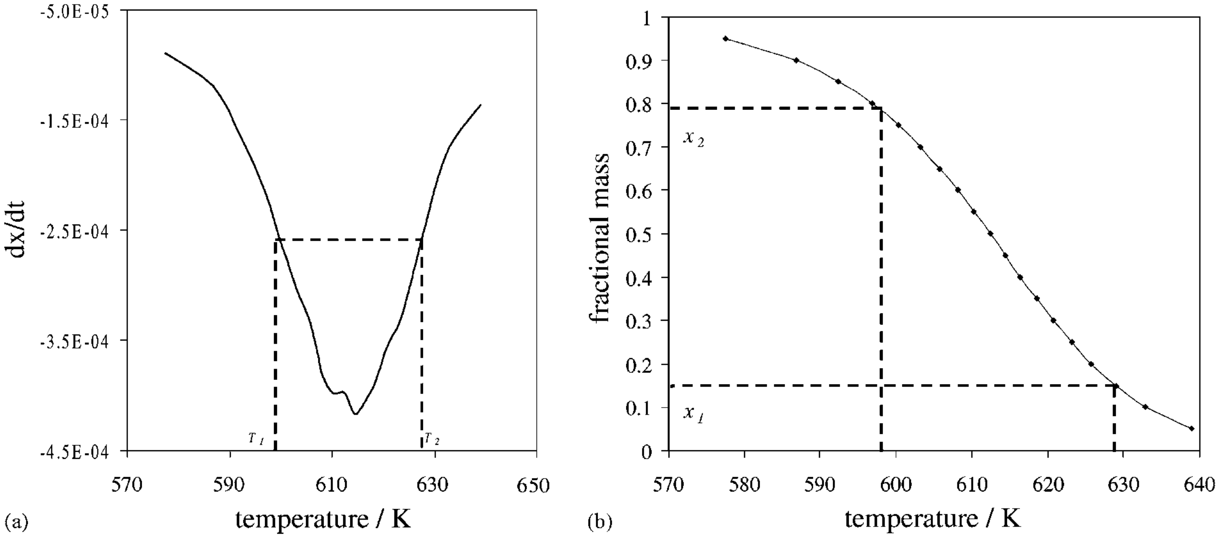

Fig. 21. Determination of the isokinetic points for PMMA.

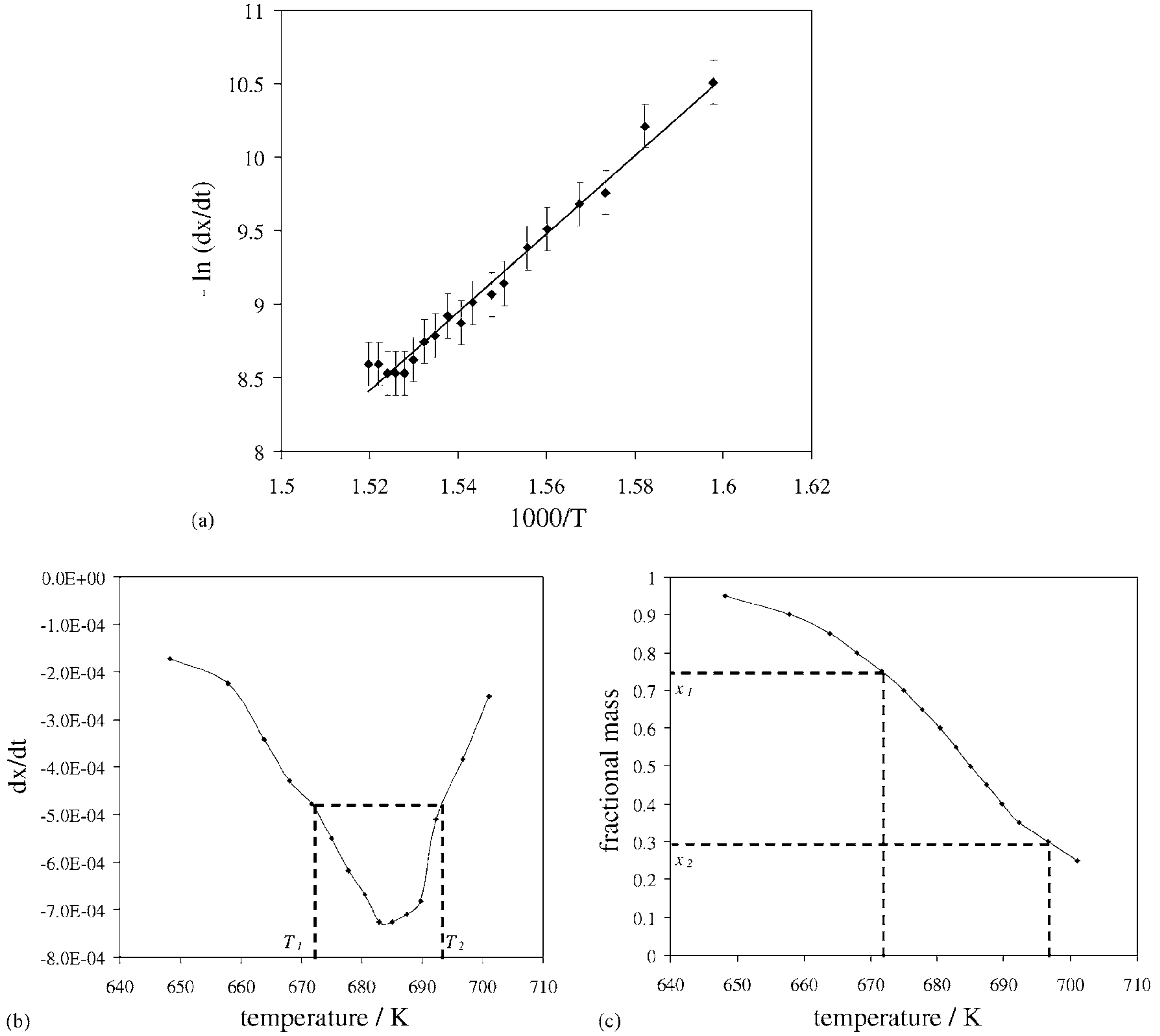

Fig. 22. Determination of kinetic parameters of PET to determine the reaction order: (a) determination of kinetic parameters at 2 °C min^{-1} and (b and c) determination of isokinetic points.

with w the residual weight, k the first-order rate constant and t the time. Also $t = \Delta T/a$, where ΔT is change in temperature from a start temperature and a the heating rate. Therefore,

$$-\ln w = \frac{kT}{a} \tag{25}$$

and using the Arrhenius expression,

$$-\ln w = \frac{T}{a} A\exp^{(-E/RT)}$$

where A is the pre-exponential factor, E the activation energy and R the universal gas constant. Hence, for a given value of T, provided that E and A are known, w can be calculated for any heating rate. The validity of this relationship was tested using non-isothermal TG data for PMMA by plotting $-\ln w$ versus $1/a$ at 340, 350 and 360 °C (see Fig. 24). In each case, good linearity was observed. The TG data for PMMA was calculated at heating rates of 1, 2, 3, 4 and 5 °C min^{-1}, using an activation energy of 210 kJ mol^{-1} and ln A

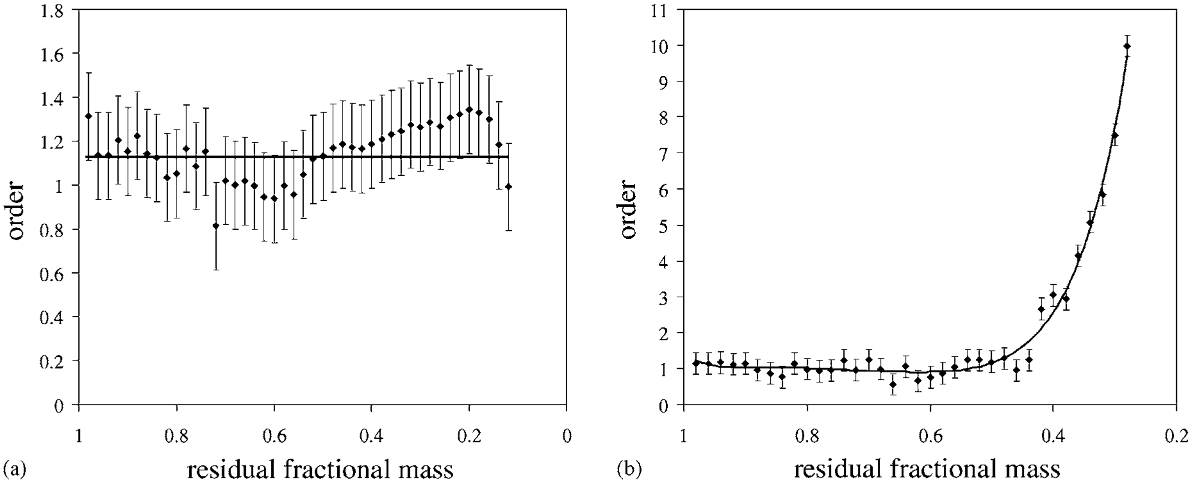

Fig. 23. Determination of reaction order for: (a) PMMA and (b) PET.

of 33.66, and superimposed upon the experimental data for PMMA, see Fig. 25. The calculated data was in good agreement with experimental data at all heating rates. However, it was found over the initial 0.40 fractional weight, that the experimental weight was greater than that computed consistent with the temperature being lower than that measured, as in thermal lag. Furthermore, it was found that over the last 0.20 fractional weight experimental was greater than that of the model. Fig. 25 gives the strong support for the temperature of the degrading sample being less than the thermocouple reading during the non-isothermal TG of PMMA and the most likely reason for this was thermal lag. Release of volatile material during thermal degradation would also cause the surface sample temperature to be reduced. The thermal degradation of PMMA has previously been found to be quite endothermic [13].

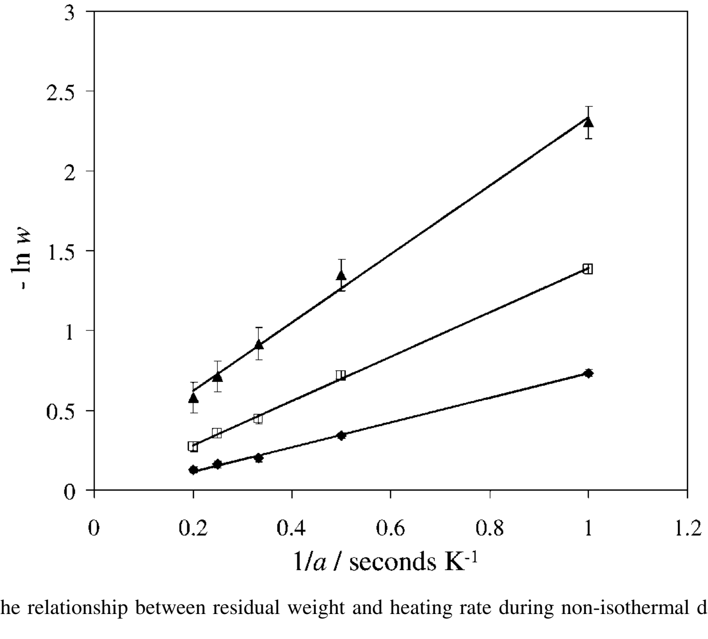

Fig. 24. The relationship between residual weight and heating rate during non-isothermal degradation.

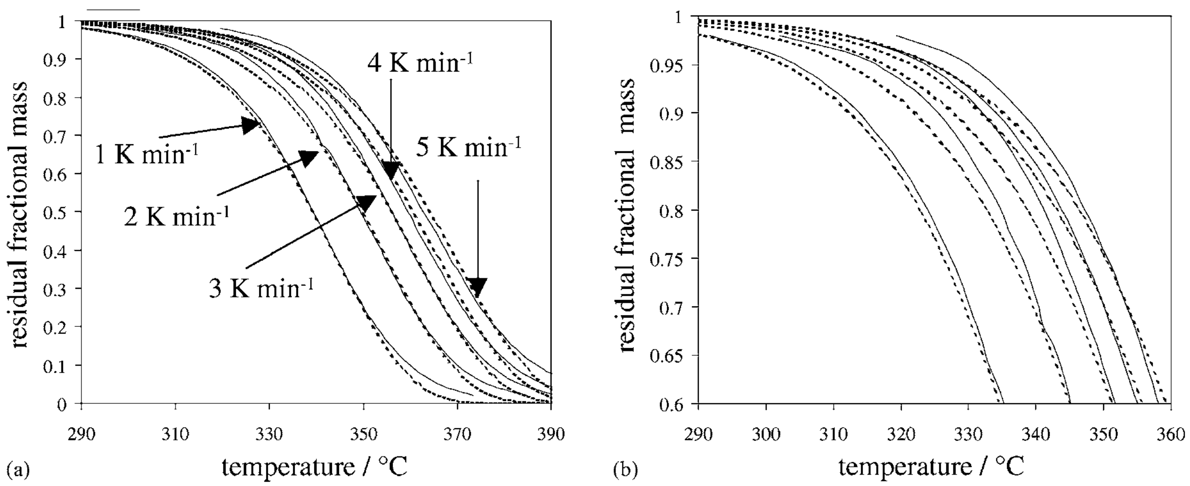

Fig. 25. The presence of thermal lag in the non-isothermal degradation: (—) experimental and (- - -) theoretical data.

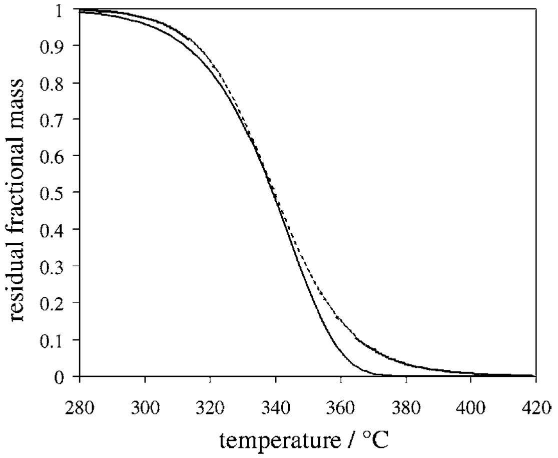

Fig. 26. Difficulty in distinguishing reaction orders in non-isothermal data: (—) first-order and (- - -) second order.

The effect of thermal lag increasing with heating rate would explain the necessity to extrapolate kinetic parameters to zero heating rate (Fig. 26).

7. Conclusions

Isothermal studies of the thermal degradation of PMMA and PET by FT-IR spectroscopy [9] have emphasised the presence of side reactions, that lead to involatile cross-linked chars and to side-group elimination from the chain as well as chain scission, which complicate the kinetics of the degradation process. This results in first-order kinetics only being observed over a limited extent of reaction. This undoubtedly limits the applicability of the non-isothermal kinetic schemes since the initial assumption of a uniform simple reaction is not valid. Despite this kinetic parameters have been derived and are listed in Table 2, and the assumptions adopted in Tables 3 and 4. All the methods described determined acceptable values for the activation energy for the decomposition of PMMA, but not for PET. Greater variations were encountered in estimating the pre-exponential factor and the reaction order.

Ozawa's method gave an acceptable estimate of the pre-exponential factor for the thermal degradation of PMMA, but not for PET. The master TG curve for PMMA fitted a first-order kinetic dependence well, and this allowed an accurate estimate of the lateral shift required for superimposition of the curves (equal to log A) to be made. However, the master TG curve of PET did not fit the theoretical first-order curve, or any other theoretical curve. It was not possible to estimate lateral shifts.

The activation energies calculated by the Coats and Redfern's method appeared to depend upon the heating rate used. This was probably due to thermal lag and it was necessary to extrapolate the activation energy to zero heating rate to obtain values closer to the isothermally determine one, although it can also be caused by incorrect determination of reaction order.

Table 2
Kinetic parameters calculated from non-isothermal TG data

Polymer	Method	Activation energy (kJ mol^{-1})	Pre-exponential factor (s^{-1})
PMMA	Isothermal	210 ± 10	$(4.15 \pm 0.42) \times 10^{14}$
	Ozawa	210 ± 10	$(8.91 \pm 0.89) \times 10^{14}$
	Coats and Redfern	210 ± 20	n.d.[a]
	Friedman	210 ± 10	Impossible to estimate due to curvature in data
	New method	200 ± 10	$(2.26 \pm 0.11) \times 10^{14}$
PET	Isothermal	220 ± 10	$(5.73 \pm 0.57) \times 10^{13}$
	Ozawa	180 ± 10	$(6.31 \pm 0.63) \times 10^{10}$
	Coats and Redfern	250–280	n.d.
	Friedman	170 ± 10	Impossible to estimate due to curvature in data
	New method	220 ± 10	$(8.63 \pm 0.43) \times 10^{13}$

[a] n.d.: not determined.

There was a large error in extrapolating to zero heating rate. The first-order plots were non-linear in both case, but more severely in the case of PET. Thus the activation energy was only calculated over the first 0.40 fractional weight loss. Coats and Redfern [2] claimed that the reaction order could be determined by finding the reaction order that gave the best linear plot. Given that at high conversion, data for PET deviated from first-order kinetics markedly the results of such an exercise are misleading.

Friedman's method gave acceptable estimates of the activation energy for PMMA, but not for PET. The estimates were lower and it was considered that the low estimate was probably due to the faster heating rates used in the thermal degradation of PET, leading to a significant amount of thermal lag. Difficulty was experienced in analysing the pre-exponential factor and reaction order, because a linear plot of ln $[A\, f(w/w_0)]$ versus ln $[(w - w_\mathrm{f})/w_0]$, could not be obtained for either PMMA or PET.

Table 3
Assumptions inherent in non-isothermal analyses of TG data

Method	Assumptions
Ozawa	Assumes no thermal lag $\int_0^T \exp\left(\frac{-\Delta E}{RT}\right) \mathrm{d}T = \frac{-\Delta E}{R} p\left(\frac{-\Delta E}{RT}\right)$ (after Doyle) $\log p\left(\frac{-\Delta E}{RT}\right) = -2.315 - 0.4567\left(\frac{-\Delta E}{RT}\right)$ ±5% provided $20 < \Delta E/RT < 50$ Production of master TG data assumes no thermal lag, and that, on average the shape of the non-isothermal TG curve does not change with heating rate, but is only displaced
Coats and Redfern	Assumes reaction order is constant and no thermal lag $\int_u^{\infty} \exp^{-u} u^{-b} \mathrm{d}u \approx u^{1-b} \exp^{-u} \sum_{n=0}^{\infty} \frac{(-1)^n (b)^n}{u^{n+1}}$ Assumes that kinetic order can be acceptably determined by finding the best straight line fit
Friedman	Assumes no thermal lag $f\left(\frac{w}{w_0}\right) = \left[\frac{(w - w_\mathrm{f})}{w_0}\right]^n$ is assumed to account for changes in kinetics due to side reactions such as non-volatile residue formation

Table 4
Assumptions inherent in non-isothermal analyses of TG data

Method	Assumptions
New method, first-order kinetics	First-order kinetics but can choose any reaction order Reaction order is constant Assumes weight loss over a very small temperature interval (≤ 1 °C) can be treated as isothermal
New method, reaction order unknown	Non-order specific method of determination of activation energy assumes no thermal lag Assumes that over first 0.10 fractional weight, differences between data of different reaction orders is small Assumes that the weight loss over a very small temperature interval (≤ 1 °C) can be treated as isothermal Method of analyses of reaction order assumes no thermal lag

The activation energies and pre-exponential factors determined by the alternative method were found to be in good agreement with isothermal TG results. Therefore, it can be concluded that the assumptions made in the analyses held in both cases. Furthermore, this was the only method that could allow for the development of thermal lag in the TG data. Given the close agreement of kinetic parameters to those obtained from isothermal data, it is recommended that this method be used to analyse non-isothermal TG data in preference to the three literature methods discussed above.

The additional analyses procedure allowed the reaction order to be determined satisfactorily. The thermal degradation of PMMA and PET were shown to be first-order over an initial limited conversion period. The reaction order of PMMA did not vary much with residual weight, although above 0.5 fractional weight, the reaction order increased but remained marginally within experimental error. Similarly, the reaction order of PET was consistently 1.0 over the first 0.5 fractional weight. However, beyond this conversion, the reaction order increased markedly. It is therefore recommended that kinetic analyses of non-isothermal data for PMMA and PET should only include the first 0.5 weight fraction of the degradation.

At the beginning, two possible advantages of kinetic analyses of non-isothermal TG over that of isothermal TG were mentioned, firstly overcoming the problem of slow temperature rise-times in isothermal TG, and secondly, the potential to calculate kinetic parameters from a single TG experiment. The problem of slow temperature rise-times in isothermal TG means that degradation of the sample may take place before the desired degradation temperature is reached, making assessment of degradation of the first few percent of the polymer difficult. In non-isothermal TG, thermal degradation can be assessed in this region, but it is susceptible to thermal lag effects. Thermal lag effects also prevent the extraction of kinetic data from a single experiment, because to overcome the thermal lag it is necessary to extrapolate to zero heating rate, for which the results of several experiments are required.

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