Kinetic analysis by repeated temperature scanning.
Part 1. Theory and methods

Takeo Ozawa

Chiba Institute of Technology, Tsudanuma 275-0016, Japan

Abstract

A repeated temperature scanning thermal analysis, such as temperature-modulated thermogravimetry, is a useful technique for the kinetic analysis of thermal decomposition in a defined temperature range. In this technique, repeated temperature scanning, i.e., cyclic heating and cooling in a defined temperature range, is introduced into thermal analysis. First, the kinetics for this new mode of temperature change are considered theoretically, and some useful relations for kinetic analysis are revealed. From these relations, methods for estimating kinetic parameters, such as the activation energy, the pre-exponential factor and the conversion functions, are derived. The errors in these parameters are also examined. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Kinetic analysis using conventional thermogravimetry (TG) and other thermal analysis techniques with a constant rate of heating has a few drawbacks, because the temperature is raised at a constant rate irrespective of the process proceeding in the sample. In some cases, especially for polymers, the reaction mechanism changes with an increase in the temperature, so that the reaction mechanism changes during the run. Controlled rate TG (CRTG, or sample controlled TG, SCTG) and isothermal TG are useful for these cases, as reported in a previous paper [1]. However, to observe the reaction in a defined temperature range, where the mechanism does not change, CRTG is not so suitable, because the temperature

tends to increase beyond the temperature limit, especially at the final stage of the run. The range of controllable mass-loss rates in CRTG is also limited, and the minimum rate is not low enough to apply CRTG to studying the low-temperature stability of materials. Isothermal TG does not have such drawback, but it takes a relatively long time, especially in a low-temperature range. For the kinetic analysis of non-isothermal data, iso-conversional methods are the only methods which can give highly reliable kinetic parameters [2], and the Friedman–Ozawa method is the most reliable and has the widest applicability among them [1,2]. However, multiple runs are needed for the iso-conversional methods, so that it takes a long time to perform the experiments.

The temperature-jump [3] and the rate-jump [4] methods were proposed for estimating the activation energy from a single run. In these techniques, the

activation energy is estimated from the rate change or the temperature change resulting from these respective jumps. The temperature range, however, cannot be defined in the rate-jump method.

Recently, temperature modulation, i.e. one of repeated temperature scanning, was introduced into TG (temperature modulated TG; tm-TG) [5–10], and sinusoidal temperature modulation has been applied. By comparing the rates of mass loss at a peak and an adjacent bottom of the temperature–time curve or by applying Fourier analysis, the activation energy is estimated during the run with good precision. This method is highly efficient, because the activation energy is continuously estimated from a single run. However, further kinetic analysis has not yet been done, and it seems difficult because of the sinusoidal temperature modulation, which does not make the calculation simple.

A method for estimation of the activation energy and further kinetic analysis by repeated temperature scanning technique is proposed in this paper. It is different from temperature modulation, though temperature modulation is an example of repeated temperature scanning. The mode of temperature change in cycles is not necessarily uniform and not necessarily controlled precisely, but can be changed during the experiment. It should be noted, in relation to this point, that the temperature control is sometimes disturbed by a large reaction heat.

In this paper, kinetic equations for repeated temperature scanning thermal analysis (rts-TA) have been derived on the base of the concepts of reduced time and reduced rate [2,11,12]. Furthermore, a method for kinetic analysis is proposed for obtaining simultaneously the activation energy, the pre-exponential factor and the conversion functions and to predict the process under different temperature changes. The new and useful point of this technique is that kinetic analysis can be done from a single run, while the method is applicable to various modes of temperature scanning. Errors in estimating the activation energy are also discussed.

Constant-rate heating TG has been used for the short-time thermal life evaluation of polymeric materials [13–15]. It is not, however, used extensively for electrical insulating materials, because the temperature range for the usual constant-rate heating TG experiment is much higher than the operating tem-

perature of electrical cables and machines in which the materials are used [16]. The reaction observed by the usual constant-rate heating TG might be different from the real reaction in this use, as seen for polyimide [1]. Thus, constant-rate heating TG is thought to be inappropriate for long-term thermal endurance evaluation [16,17]. Because rts-TG observes the reaction in a defined temperature range, it is better for evaluating real thermal endurance of the materials.

It is the purpose of this series of papers to propose a new kinetic method for rts-TA and to evaluate this applicability. It should be noted that the theory and the method described in this paper can also be applied to other physical processes, such as thermal shrinkage of polymer film and crystalline growth from pre-existing nuclei, though the Arrhenius law does not always hold in these cases.

2. Theoretical consideration

In this paper, we deal with only a single elementary process, and the physical property observed in the thermal analysis is a single-value function of the changing species or the formed structure. It is also assumed that the Arrhenius law holds for the process, namely,

$$C = f(\alpha) \tag{1}$$

and

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) g(\alpha) \tag{2}$$

where α, C, t, A, E, R and T are, respectively, the extent of the process, the conversion of the physical property, the time, the pre-exponential factor, the activation energy, the Universal Gas Constant and the absolute temperature, and $f(\alpha)$ and $g(\alpha)$ the conversion functions of α expressing the dependence of the physical property on the extent of process and the mechanism. (The forms of these functions for some cases are listed in Ref. [12].) The conversion and the extent of the process are, in most cases, equal to each other but, for instance, the sample mass, m, in random scission in the main chain of polymer is a function of the fractional bonds broken, α, so that Eq. (1) is necessary. Provided that the process we deal with follows these equations, the following relation holds for a certain conversion

function [1,12]:

$$\frac{dC}{dA\theta} = g'(C) \tag{3}$$

or

$$\frac{dC}{d\theta} \equiv \left(\frac{dC}{d\alpha}\right)\left(\frac{d\alpha}{d\theta}\right) = Ag'(C) \tag{4}$$

where θ is the reduced time which equals $\int \exp(-E/RT)\, dt$ [1,9,10] and $dC/d\theta$ is the reduced rate, while $(dC/dA\theta)$ is a generalized, dimensionless rate. The function, $g'(C)$ is a function of C and the product of $df(\alpha)/d\alpha$ and $g(\alpha)$, and is characteristic of $g(\alpha)$ and $f(\alpha)$. On the other hand, the real rate is related to the reduced rate as in the following equation:

$$\frac{dC}{d\theta} \equiv \left(\frac{dC}{dt}\right)\left(\frac{dt}{d\theta}\right) = \exp\left(\frac{E}{RT}\right)\frac{dC}{dt} \tag{5}$$

These relations (namely, Eqs. (3)–(5)) hold at any point (any time, any conversion, any rate, etc.) during any temperature change. Therefore, when we plot the experimental data in the form of $dC/d\theta$ vs. C (Eqs. (4) and (5)), it is the experimental master curve. On the other hand, the relation between the generalized, dimensionless rate, $(dC/dA\theta)$, and the conversion, C, is a theoretical curve characteristic of $g(\alpha)$ and $f(\alpha)$ (Eq. (3)). These two curves correspond to each other, provided that the model (Eqs. (1) and (2)) holds in the process under observation. Thus, we can determine $g(\alpha)$ and $f(\alpha)$ from the form of the curve [12].

Conversely, the above consideration can be applied to rts-TA data by changing the temperature between definite peak and bottom temperatures. When we plot the experimentally observed rate (dC/dt) against the conversion (C), the envelope connecting the rate at the constant peak temperature is equivalent to the curve of the isothermally observed rate vs. the conversion at this temperature (Eqs. (4) and (5)). The envelope connecting the rate at the bottom temperature is also equivalent to the curve of the isothermally observed rate vs. the conversion at the bottom temperature. It is the same for a given intermediate temperature between the peak and the bottom temperatures.

In other words, the rate in rts-TA oscillates between these envelopes, and this oscillatory trace is governed by the essential relation among the generalized, dimensionless rate, the conversion and the generalized, dimensionless time (Eq. (3)), and also deter-mined by the experimental conditions. This essential relation is characteristic of $f(\alpha)$ and $g(\alpha)$, and the envelopes are equivalent isothermal curves. The rts-TA results are illustrated in Fig. 1, where the mass-loss rate in rts-TG for polyimide is shown against the time. The mass-loss rates at the peak and bottom temperatures are plotted against the mass loss in Fig. 2 together with the master curve for this decomposition reported in the previous paper [1]. The envelopes are quite similar to the master curve. When the ordinate is converted to the logarithm of the rate, the vertical distance is dependent on the activation energy and the temperature of the envelope, because the activation energy does not changed along with the conversion [1].

In view of the reduced time being a fundamentally important quantity for non-isothermal kinetics and useful for predicting the reaction under isothermal and/or non-isothermal conditions [1,11,12], the reduced time in rts-TA of a constant temperature cycle is considered below. It can be calculated easily for sawtooth temperature modulation (triangular scanning), because of additivity of the reduced time. For instance, the reduced time $\theta_{p,n}$ at the nth peak is given below:

$$\theta_{p,n} = Ep\left(\frac{E/RT_h}{\beta R}\right) + (n-1)\theta_c \tag{6}$$

where β, p, T_h and θ_c are, respectively, the initial heating rate, the p-function proposed by Doyle [18], the peak temperature and the reduced time for one cycle. The reduced time for one cycle, θ_c is as follows:

$$\theta_c = 2E\frac{p(E/RT_h) - p(E/RT_l)}{\beta' R} \tag{7}$$

or

$$\theta_c = PE\frac{p(E/RT_h) - p(E/RT_l)}{R(T_h - T_l)} \tag{8}$$

where β', P and T_l are, respectively, the heating and cooling rates in the cycle, the period for one cycle and the bottom temperature. The cooling rate is not necessarily equal to the heating rate, but it is better to use the same rates for simplicity. Similarly, the reduced time at the nth bottom, $\theta_{b,n}$, is given below:

$$\theta_{b,n} = \Delta Ep\left(\frac{\Delta E/Rt_h}{\beta R}\right) + (n-0.5)\theta_c \tag{9}$$
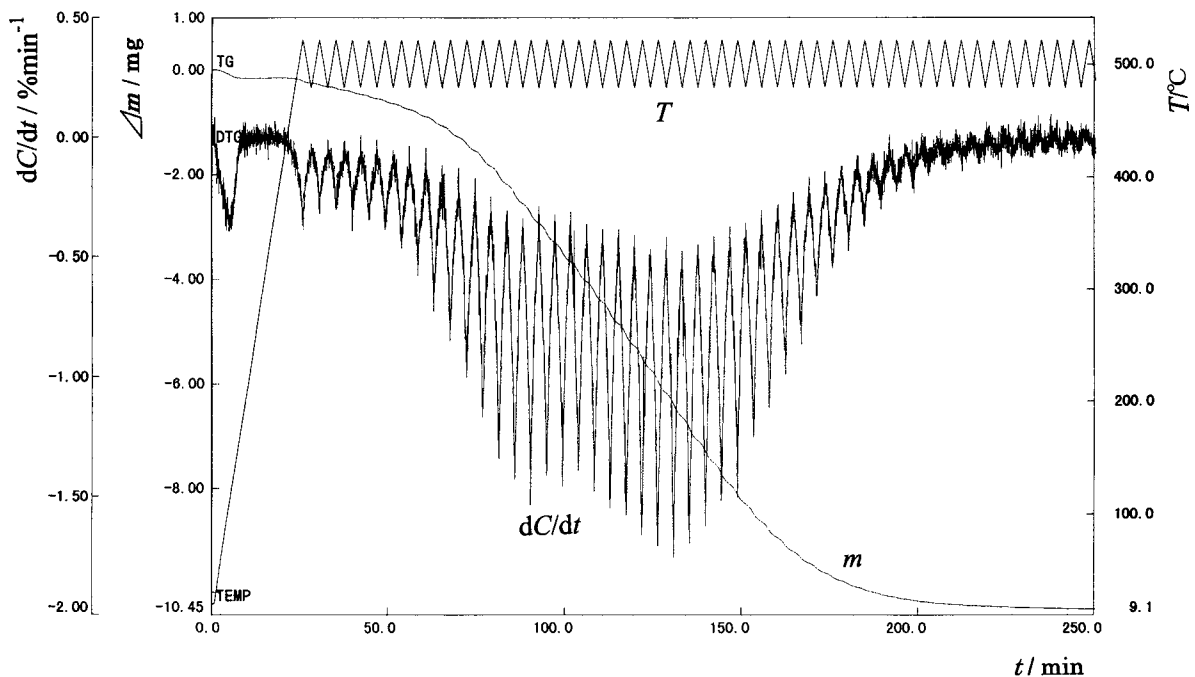
Fig. 1. Repeated temperature scanning TG curve of polyimide. The TG was done under a flow of standard air at 200 ml/min, and the temperature was repeatedly scanned between 480 and 520°C at a constant rate of 20°C/min. The symbol $\triangle m$ is the mass loss.

As seen above, the reduced time is approximately proportional to the real time in the experiment. Therefore, the envelopes of the measurements at the peak and the bottom temperatures, i.e. the curves of rate vs. real time are approximately equivalent to the isothermal curves of rate vs. time in their form.

When a constant temperature mode is combined with the above cyclic temperature change, the reduced time is the sum of these two temperature modes. The reduced time θ_{iso} is given below:

$$\theta_{\mathrm{iso}} = d \exp\left(-\frac{E}{RT}\right) \tag{10}$$

where d is the duration of the constant temperature mode.

The reduced time for a sinusoidal temperature modulation is difficult to calculate, but the reduced time for one cycle is constant for any mode of modulation, so that the situation is similar for the sinusoidal temperature modulation and other modes of temperature modulation.

3. Methods for kinetic analysis

As mentioned above, the envelopes are very useful for kinetic analysis. First of all, we can determine the conversion functions from the form of the envelopes when we transform the results to the form of rate vs. conversion. For instance, straight lines are obtained for a first-order reaction, because $C=\alpha$ and $g(\alpha)=1-C$. Secondly, when we plot the logarithm of the rate from the envelopes against conversion, these logarithmic envelopes can be superimposed on each other by a vertical shift (see Eq. (5)). The shift distance is in a linear relation with the reciprocal absolute temperature, the slope being $-E/R$. These logarithmic envelopes can also be superimposed on the theoretical curve of the logarithm of $(\mathrm{d}C/\mathrm{d}A\theta)$ vs. C, the vertical shift distance giving $A \exp(-E/RT)$. Thus, we have all the kinetic parameters necessary to predict the process under study. The master curve, C vs. θ, for prediction can be derived by using the theoretical relation of C with $A\theta$ for the conversion functions of $g(\alpha)$ and $f(\alpha)$. Otherwise, the reduced time can also be calculated by
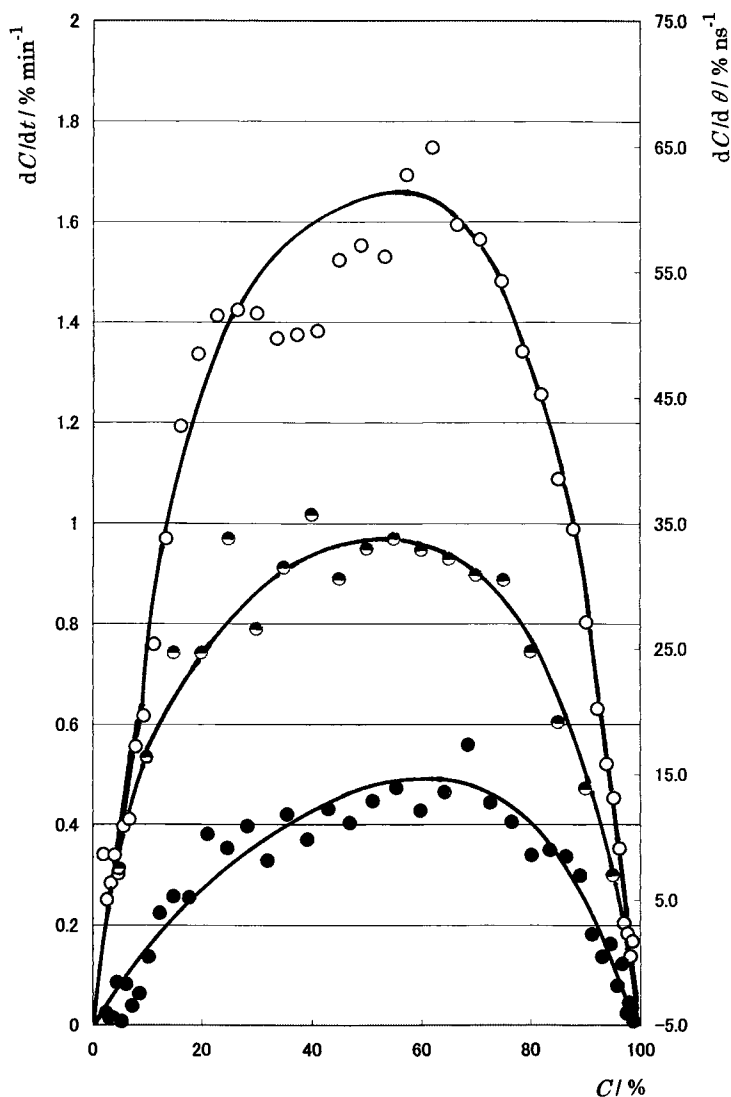
Fig. 2. The relation between mass-loss rate and mass loss at 520°C (○) and 480°C (●) by transformation of the data in Fig. 1, and the master curve (◑) of reduced mass-loss rate vs. mass loss for polyimide [1].

using E and the real temperature change along with the time (Eqs. (6) and (9)), if the temperature change is not too complicated.

When we use temperature scanning in which multiple peak and bottom temperatures occur in one cycle, we can see the temperature dependence of the rate in more detail. For instance, when the temperature scanning cycle consists of heating from T_a up to T_b, then cooling to T_c and heating to T_d followed by cooling to T_a, we have two peak temperatures, T_b and T_d, and two

bottom temperatures, T_a and T_c, so that we have the equivalents of four isothermal curves at different temperatures. When we measure the rate as a function of the conversion at some selected intermediate temperatures, we obtain similar results.

From the above vertical shift and the superposition, we can confirm the Arrhenius law from the linearity between the vertical shift distances and the reciprocal absolute temperatures. Because we have more than two equivalent isothermal curves, we can

estimate the activation energy more accurately. The principle of the above procedures is the same as the Friedman–Ozawa plot [2], so that this method can be applied to interpolated rates of conversion together with experimentally measured rates of conversion at a given conversion.

The above procedure for kinetic analysis can be done by linear multiple regression analysis. Combining Eqs. (4) and (5) and taking the logarithms, we have

$$\ln \frac{dC}{dt} = \ln A - \frac{E}{RT} + \ln g'(C) \qquad (11)$$

Thus, $\ln dC/dt$ is expressed by a linear polynomial equation of C, and linear multiple regression analysis can be applied to sets of data (dC/dt, C and T). The particular form of $g'(C)$, for which the ratio of the contribution is the largest amongst the tested conversion functions, is the best fitted one, and A and E are the corresponding kinetic parameters.

The activation energy can also be estimated during the run by a method, similar to the methods for the temperature or rate jump techniques and tm-TG. By comparing the maximum mass-loss rate at the peak temperature and the minimum mass-loss rate at the adjacent bottom temperature (or vice versa), the following equation is used to estimate the activation energy [3,4,5]:

$$E = R t_h T_l \ln \left(\frac{r_h/r_l}{T_h - T_l} \right) \qquad (12)$$

where r_h and r_l are the rates of conversion (dC/dt) at the peak and at the bottom temperatures, respectively. To estimate the activation energy more accurately, the following rates averaged for the peaks or the bottoms at the same temperature should be used in the actual calculation. For the cycle from the ith peak to the ($i+1$)th peak, the average rate used is as follows:

$$r_h = \frac{r_{h,i} + r_{h,i+1}}{2} \qquad (13)$$

This is compared with $r_{l,i}$. Similarly, for the cycle from the ith bottom to the ($i+1$)th bottom,

$$r_l = \frac{r_{l,i} + r_{l,i+1}}{2} \qquad (14)$$

These plots are also based on the same principle as the Friedman–Ozawa plot.

4. Discussion

The most reliable methods for kinetic analysis of thermoanalytical data are the iso-conversional methods [2]. Among the iso-conversional methods, the Ozawa–Flynn–Wall plot and the Kissinger–Akahira–Sunose plot are integral methods. In these plots, the relation between the conversion and the reduced time (integration of the temperature) forms the basis of the methods; moreover, approximate integral equations for the constant rate heating are used. The methods, therefore, only apply to constant heating rate experiments.

On the other hand, the iso-conversional Friedman–Ozawa plot [2] is a differential method, and the previous thermal history of the sample does not influence the plot of the logarithmic rate vs. the reciprocal absolute temperature at a given conversion. Therefore, this plot can be applied to data obtained by any mode of temperature change including CRTG and isothermal TG as demonstrated in a previous paper [1]. Moreover, no approximations are used in this plot. The methods proposed in this paper are essentially the same as the Friedman–Ozawa plot in combination with the repeated temperature scanning. The methods in this paper could thus be called quasi-iso-conversional methods. Because equivalent isothermal curves of rate vs. conversion are obtained by the transformation, the method is also equivalent to isothermal methods.

The name, quasi-iso-conversional methods, comes from the fact that quantities such as the rate and conversion, are not only the experimentally measured ones but also those estimated by interpolation. Errors caused by this interpolation need to be considered. A short temperature cycle is preferable in order to decrease the error, but, as discussed elsewhere, for temperature oscillation in differential scanning calorimetry (tm-DSC) [19–21], when the temperature wave propagates in the apparatus and the sample, a decrease in the amplitude and a shift of the phase necessarily occur. Thermal contact between the sample cell and the apparatus has the same serious effect. A large amount of the sample and poor thermal contact of the sample with the cell cause a large decrease in the amplitude and a large shift of the phase. Because the controlled temperature in thermal analysis apparatus is not the sample temperature, but that of the tem-

perature sensor, the sample temperature does not follow the temperature program exactly, especially in a short-cycle program. The temperature distribution necessarily occurs also in constant-rate heating and cooling, as clearly elucidated before for differential thermal analysis [22,23]. High rates of heating and cooling cause large temperature lags. These effects are not detected directly, but need to be taken into account. Thus, there should be an optimum cycle, and too sharp a temperature change is not desirable. Furthermore, a small sample heat capacity and a large heat-transfer coefficient are preferable, because the thermal response time is proportional to the sample heat capacity and inversely proportional to the heat-transfer coefficient [19–23]. Thus, a short distance from the sample to the temperature sensor is also desirable for the control and measurement.

It should be noted that when Fourier analysis is applied to tm-TG by sinusoidal modulation [5], errors must be introduced because of the non-linear temperature dependence of the rate constant. The acceleration effect above the average temperature of the modulation is not the same as the deceleration effect below the average temperature. Thus, the modulated rate is a deformed sinusoidal oscillation containing higher harmonics, even if the temperature modulation is exactly sinusoidal. There is another cause for deformation, i.e. a small change in the conversion. Considering these effects, a large amplitude of temperature modulation causes a large error. A small amplitude is preferable and the effect is much more detectable in the low-temperature range because of the nature of the Arrhenius equation. For example, for a temperature modulation of 10°C amplitude at an average temperature of 500°C and an activation energy of 350 kJ/mol, the decelerating effect is not very different from the accelerating effect, and the non-linearity is not detectable, but a large amplitude in a relatively low-temperature range is not recommended. Therefore, Fourier analysis of temperature modulation is not suitable for wide temperature scanning.

The imaginary part in the Fourier analysis should also be discussed. It has been thought that the rate changes instantaneously as the temperature changes. Therefore, it seems likely that the observed imaginary component of the Fourier analysis is not caused by the kinetic effect, but by the temperature wave propaga-

tion, as mentioned in the foregoing. Consideration by analogy with tm-DSC tends to lead to a misunderstanding, and we should consider the phenomena occurring in the experiment in more detail.

The acceleration and the deceleration effects mentioned above are made clear from Eq. (8) by comparing θ_c with another reduced time, θ_{iso}, which is the reduced time of the isothermal process for P at the average temperature T_{av} [$=(T_h+T_l)/2$], because the reduced time is a measure of the extent of the process. The comparison is.

$$\frac{\theta_c}{\theta_{iso}} = E\frac{p(E/RT_h) - p(E/RT_l)}{R(T_h - T_l)\exp(-E/RT_{av})} \qquad (15)$$

where θ_{iso} is given by

$$\theta_{iso} = P\exp\left(\frac{-E}{RT_{av}}\right) \qquad (16)$$

Examples are shown in Table 1 [24]. The larger the activation energy and the temperature range are, the larger the overall deceleration effect is. This is also clear evidence of the non-linear temperature dependence of the rate constant. This suggests that concurrently proceeding multiple processes of different activation energy may be separated by repeated temperature scanning, especially in a low-temperature range.

For complex processes, the fundamental Eqs. (1) and (2) do not hold in observed processes. In these cases, the relation between dC/dt vs. C at the peak temperature is different from that at the bottom temperature, and the superimposition by the vertical shift mentioned above cannot be achieved. When these relations are observed at more than two temperatures, the vertical shift distance is not in linear relation with the reciprocal absolute temperature. The estimated activation energy thus changes with the conversion

Table 1
Comparison in extent of process between isothermal run and repeated scanning run

E(kJ mol^{-1})	T_h ($^\circ$C)	T_l ($^\circ$C)	T_{av} ($^\circ$C)	θ_c (θ_{iso})
62.7	200	160	180	0.93
83.6	200	160	180	0.87
104.5	200	160	180	0.80
125.4	200	160	180	0.73
146.3	200	160	180	0.66
167.2	200	160	180	0.59

and is the apparent activation energy. These results indicate the complexity of the process under study.

The essential point of this new technique is not the temperature modulation, but the repeated temperature scanning. By a simple repeated temperature scanning, we can obtain by interpolation the isothermal relations between the rate and the conversion at different temperatures.

5. Conclusion

1. Rts-TA is useful for estimating the activation energy, the pre-exponential factor and the conversion functions, especially in a defined low temperature range. It is also a time saving technique, because the kinetic analysis can be done using data from a single run. Rts-TA seems especially useful for polymers and organic substances, because the mechanism might change with the temperature for these substances.

2. The essential points of the method proposed in this paper are: (1) to transform the rts-TA results to the form of rate vs. conversion; (2) to get equivalent isothermal curves by connecting the points at a few temperatures; (3) to determine the conversion functions; (4) to estimate the activation energy and the pre-exponential factor by a quasi-iso-conversional method; and (5), if needed, to transform the data to a useful experimental master curve of the conversion or the reduced rate vs. the reduced time.

3. Rts-TA and the kinetic methods proposed in this paper have advantages over tm-TG and its kinetic method, because of their wider applicability and yet all the necessary kinetic information can be obtained. Transformation of the data to the form of the rate vs. the conversion is the essential point, and by this transformation the method becomes precise and applicable to a wide temperature range. The temperature mode is also not restricted.

The experimental verification of this method is now underway in our laboratory and the results will be described in the next paper to be submitted to this journal.

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