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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

CONTROLLED RATE THERMOGRAVIMETRY
New usefulness of controlled rate thermogravimetry revealed by decomposition of polyimide

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Abstract

Curves obtained by controlled rate TG of polyimide film in air are quite different from those obtained by conventional constant rate heating TG. A two step mass loss was observed during the constant rate heating TG, while mass loss proceeded as a single step process in the controlled rate TG. To elucidate the cause for this difference, kinetic analysis was made, and it was found that the reaction mechanism in a lower temperature range is different from those in a higher temperature range. The lower temperature decomposition is a single step process, and the higher temperature decomposition is a two-step process. The reason for the difference is that only the low temperature single step process is observed in the controlled rate TG, while both reactions are observed in the constant heating rate TG along with the temperature increase. This speculation was confirmed by isothermal TG. These facts show us another usefulness of controlled rate TG. To analyze the three types of TG data together, the Friedman–Ozawa method was used, and it is demonstrated to be the most appropriate and reliable.

Keywords: CRTG, Friedman–Ozawa method, isothermal-TG, kinetic analysis, polyimide, TG, thermal decomposition

Introduction

It was a few decades ago that controlled rate thermal analysis (CRTA) was invented independently by Rouquerol and Paulik *et al*. [1]. However, its applications have not been made so often until recently, presumably because of difficulty in controlling the rate of reaction. Now that commercial instruments of CRTA are available, it is now applied to many fields, such as dehydration processes, solid reactions and sintering, and its high temperature resolution has drawn much attention.

The present author applied controlled rate thermogravimetry (CRTG) to decomposition of a typical heat resistant insulating material, polyimide film, and found that the curves from CRTG are quite different from those obtained in conventional linear heating TG at a constant rate (LHTG). A single step mass loss was observed by CRTG, but two-step mass loss was recorded by LHTG. Kinetic analysis of both types of curves revealed that the reaction proceeding in a lower temperature range differs from those in a higher temperature range. The low temperature reaction is a single

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step process, and the high temperature reaction is a two-step decomposition. By CRTG we observe only the lower temperature reaction, but by LHTG both of the reactions are observed during the temperature increase. This postulate was verified by isothermal TG runs (iso-TG) at lower temperatures and higher temperatures.

In this paper the TG results are reported and this new applicability of CRTG and its combined use of iso-TG together with conventional LHTG are described. To make full use of potential capability of these techniques, those data obtained by different modes of temperature change should be kinetically analyzed by a common method. For this purpose a method proposed by Friedman [2] and expanded later by the present author [3, 4] is a single reliable one, and application of the method for this purpose is demonstrated in this paper. By this method the nature of the above thermal behavior was made clear.

Experimental

The thermobalance used in this research is a TG-differential thermal analysis (DTA) simultaneous apparatus (Thermo Plus 8120, Rigaku Denki Co., Ltd.), in whose computer the software for CRTG is installed. The sample pan is made of stainless steel net to keep atmospheric air flowing around the specimen film. Standard air in a cylinder is supplied to the thermobalance at a rate of 200 ml min^{-1}. The sample is polyimide (Kapton 500H) kindly supplied by Toray DuPont Co., Ltd. and it was used as received.

Results and discussion

A typical TG-DTA curve obtained at 10°C min^{-1} is reproduced in Fig. 1, where m, T, ΔT and t are respectively the mass, the temperature, the temperature difference in DTA and the time. An inflection point can be seen in the mass loss curve, while two large exothermic peaks are recorded in the DTA curve correspondingly. Similar TG-DTA curves are obtained at 5 and 20°C min^{-1}. The mass loss conversions at the minimums between the DTA peaks are 37% at 598°C, 35% at 617°C and 33% at

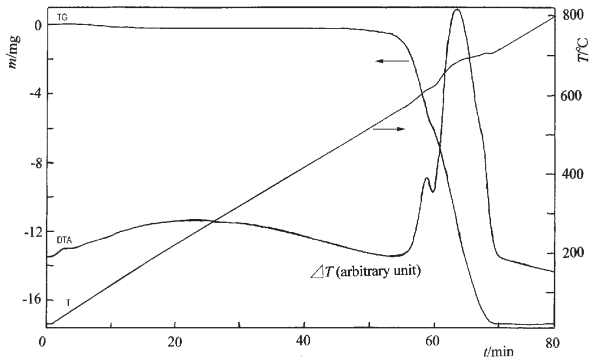

Fig. 1 Conventional LHTG curve and DTA curve of polyimide in air at 10°C min^{-1}

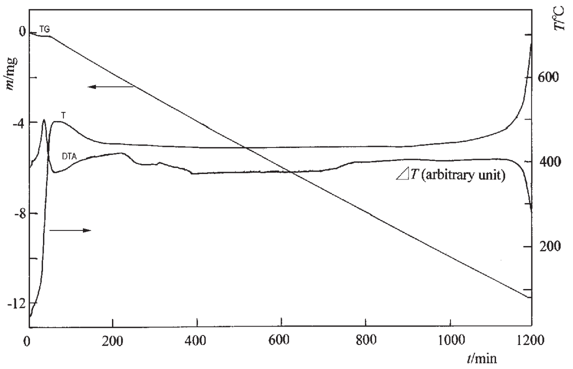

Fig. 2 CRTG curve of polyimide in air obtained at mass loss rate of 0.06% min^{-1}. The temperature difference by DTA is also shown

653°C, respectively, for 5, 10 and 20°C min^{-1}, and the mass loss reaches 100% at its final point.

On the other hand, quite different behavior was observed by CRTG as shown in Fig. 2. For keeping the mass loss rate at 0.06% min^{-1}, the temperature was changed smoothly as seen in the figure and there is no discontinuity, such as the inflection point, up to 100% mass loss. Similarly in the DTA curve no distinct peaks are observed, though the heat flow must be small as expected by the low reaction rate in the low temperature. CRTG was made at different constant mass loss rates (0.6, 0.36, 0.03 and 0.018% min^{-1}), and the curves obtained are quite the same as those in Fig. 2 in their nature. Controlling the mass loss rate at 3% min^{-1} was difficult, and the mass loss rate was controlled not so smoothly, but the curves obtained are quite the same as those by LHTG. In the DTA curve two sharp exothermic peaks are observed, and the temperature was controlled around 580°C, but a small stepwise change of the temperature was observed around the minimum between the two exothermic DTA peaks. This stepwise change indicates the change of the reaction.

To elucidate causes for this discrepancy, kinetic analysis was made. The method should be described first. The most reliable kinetic methods are iso-conversion methods [4], i.e., Ozawa–Flynn–Wall method, Kissinger–Akahira–Sunose method and Friedman method expanded by the present author. Because we must treat two different types of data, i.e., data by LHTG and CRTG, we could not use the Ozawa–Flynn–Wall plot and the Kissinger–Akahira–Sunose plot, but the expanded Friedman plot (or Friedman–Ozawa method) should be applied. The methods of Ozawa–Flynn–Wall and Kissinger–Akahira–Sunose are integral methods, so that the constant rate heating is one of the prerequisites, and these methods can not be applied to the data by CRTG. On the other hand, the Friedman–Ozawa method is a derivative method and it can be applied to data obtained by all modes of temperature change. This plot was proposed first by Friedman for n^{th} order reactions [2]. Later the present author elucidated that it can be applied generally to all types of process [3], provided that the physical properties we observed by thermal analysis is dependent only upon the amount of reacting species and the reaction proceeds by a single elementary process. Namely,

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

and

$$\mathrm{d}x/\mathrm{d}t=kg(\mathrm{x}) \tag{2}$$

where C, x and k are respectively the conversion of the physical property, the amount of reacting species and the rate constant, and $f(x)$ and $g(x)$ are functions of x; the former is a single value function of x and the latter expresses the reaction mechanism. By differentiating Eq. (1) and introducing Eq. (2) into it, we have

$$\mathrm{d}C/\mathrm{d}t=(\mathrm{d}C/\mathrm{d}x)\ (\mathrm{d}x/\mathrm{d}t) \tag{3}$$

$$=k(\mathrm{d}C/\mathrm{d}x)\ g(x) \tag{4}$$

At a given conversion of the physical property (the iso-conversion method), $(\mathrm{d}C/\mathrm{d}x)$ $g(x)$ is constant, so that when we plot the logarithm of the rate of the property change, $\mathrm{d}C/\mathrm{d}t$, *vs.* the temperature, we can get relative temperature dependence of the rate constant, k. When the Arrhenius law holds for the rate constant and the logarithm of the rate of the property change, $\mathrm{d}C/\mathrm{d}t$, is plotted *vs.* the reciprocal absolute temperature, we get a straight line and the activation energy from its slope.

The present author proposed a method for further kinetic analysis [3] by introducing a concept of reduced time, θ [5], and for the rate constant of Arrhenius type temperature dependence it is as follows;

$$\theta=\int\exp(-\Delta E/RT)\mathrm{d}t \tag{5}$$

where ΔE and R are the activation energy and the gas constant, respectively. The reduced time has the dimension of time and it is equal to the time for hypothetical reac-

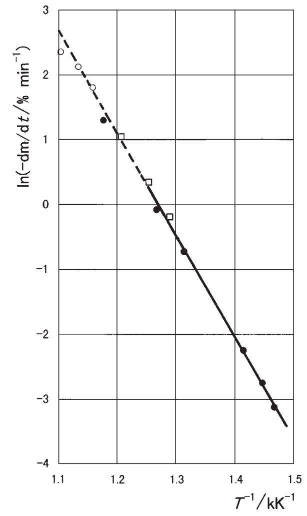

Fig. 3 Plot of logarithm of the mass loss rate *vs*. reciprocal absolute temperature for 25% mass loss conversion of polyimide. The symbols, o, • and □, are respectively LHTG, CRTG and iso-TG

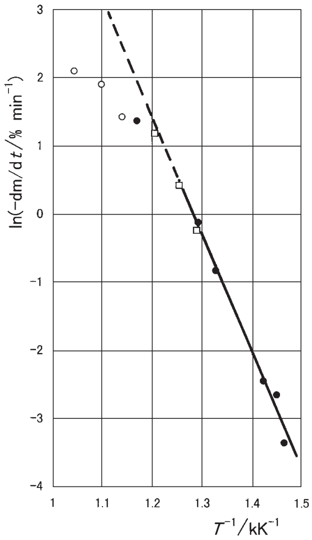

Fig. 4 Plot of logarithm of the mass loss rate *vs*. reciprocal absolute temperature for 35% mass loss conversion of polyimide. The symbols, o, • and □, are respectively LHTG, CRTG and iso-TG

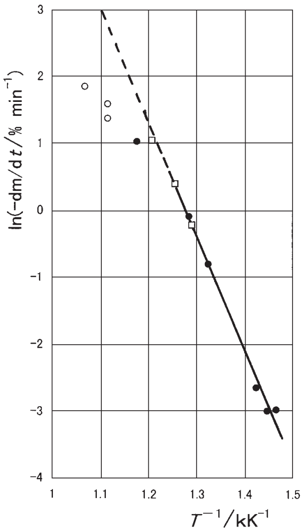

Fig. 5 Plot of logarithm of the mass loss rate *vs*. reciprocal absolute temperature for 40% mass loss conversion of polyimide. The symbols, o, • and □, are respectively LHTG, CRTG and iso-TG

tion proceeding at an infinite temperature, so that it is proportional to the time for isothermal reaction. The reduced rate, $dC/d\theta$, derived as below is a function of the conversion, which is independent of the experimental conditions, and the function

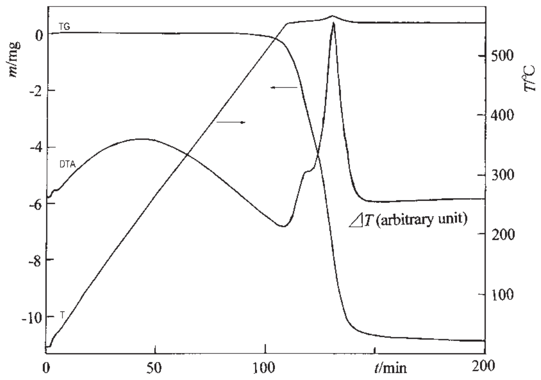

Fig. 6 Isothermal TG curve of polyimide at 550°C. The temperature difference by DTA is also shown

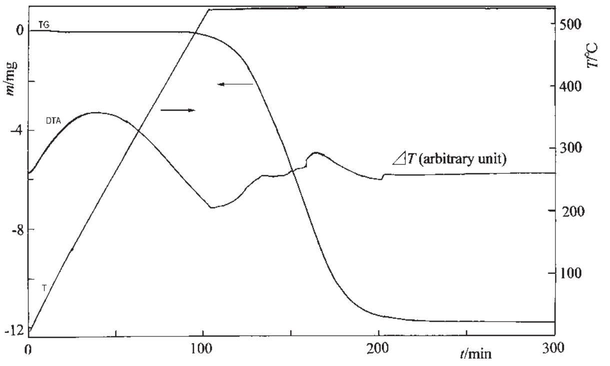

Fig. 7 Isothermal TG curve of polyimide at 520°C. The temperature difference by DTA is also shown

expresses the reaction mechanism, $g(x)$, and the relation between the conversion and the reacting species, $f(x)$ [Eq.(1)].

$$dC/d\theta = \exp(\Delta E/RT)dC/dt \qquad (6)$$

By using the estimated activation energy and the above equation, we can get an experimental master curve of the reduced rate *vs.* the conversion. In this relation we should introduce a new concept, the dimensionless reduced rate, $dC/dA\theta$, where A is the pre-exponential factor. Because the relation between the conversion *vs.* the dimensionless reduced rate can be calculated theoretically, we can determine the reaction mechanism, $g(x)$, and the relation between the conversion and the reacting species, $f(x)$, by comparing the theoretical curve with the experimental master curve.

By applying this method we get linear relations of the logarithm of the mass loss rate *vs.* the reciprocal absolute temperature at every 5% of the conversion. Three typical results are shown in Figs 3, 4 and 5, where the data by isothermal TG described below are also plotted. It is made clear from these plots that the deviations of the plots from the

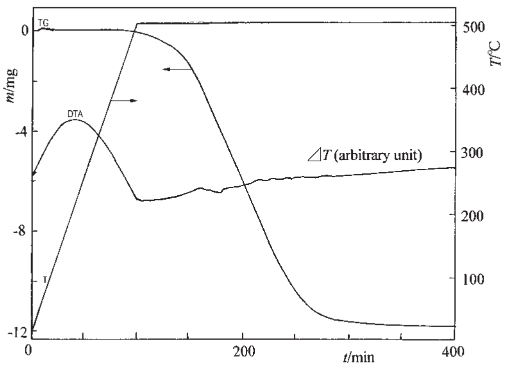

Fig. 8 Isothermal TG curve of polyimide at 500°C. The temperature difference by DTA is also shown

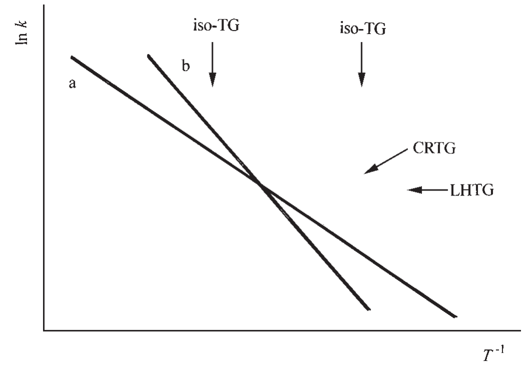

Fig. 9 Schematic drawing of temperature dependence of rates of parallel reactions for explanation of mechanisms. The arrows indicate the direction of temperature change in the experiments

straight lines are observed approximately above 500°C, and these facts suggest us that the reaction mechanism may change in a temperature range from 500 to 600°C.

To make this clear, isothermal TG runs were made at 570, 550, 520 and 500°C, and some of the results are reproduced in Figs 6, 7 and 8. As is clearly seen in Fig. 6 obtained at 550°C, an inflection point can be detected in the mass loss curve and two endothermic peaks are observed. Iso-TG curve at 570°C is also the same. However, in Figs 7 and 8 a single step mass loss is seen and distinctive peaks are not observed. Thus the cause for the discrepancy in decomposition behavior observed by LHTG and CRTG is made clear.

As seen above, by iso-TG we can observe the reactions strictly at the constant temperature except for the initial heating period, and it is more desirable observation than the other two. However, CRTG is useful and convenient, because we can observe the reaction automatically at an appropriate and desirable rate of the process by properly adjusting the temperature.

Two possibilities can be thought for the above process, and they are illustrated in Fig. 9, where two reaction rate constants are shown. One possibility is that the low temperature reaction (the line a) is a one step mass loss and the other (the line b) is a two-step mass loss. The other possibility is that the mass loss reaction proceeds by two steps in the whole temperature range, and the line b is for the reaction of the original sample forming the intermediate product, while the line a is the reaction of the intermediate to the final gaseous product. Thus, the intermediate forming reaction is the rate-controlling reaction in the low temperature range, so that the mass loss proceeds in a single step. In this possibility the activation energy for the beginning of the reaction is the same for the low temperature reaction and the high temperature reaction, and it is that for the intermediate forming reaction. As seen in the figures, this is not the case but the former possibility is the case.

The results by the isothermal TG are also plotted in Figs 3, 4 and 5. The straight lines were drawn using the data below 520°C, because it is certain that the data below 520°C are those for the lower temperature reaction. By the least square method, the activation energies were estimated from the slopes, and they are tabulated in Table 1. It should be noted that the plots for isothermal TG at 550°C are on the straight lines, so that it can be concluded that even at this temperature the low temperature reaction is still predominant over the other, though a distinctive inflection point can be detected in the iso-TG curve. Around this temperature is a transient region where two reactions proceed concurrently and one reaction mechanism is becoming predominant over the other along the temperature.

As further kinetic analysis, the experimental master curve was drawn using the average activation energy in Table 1, and it is shown in Fig. 10. The reduced rate, d*C*/dθ, was calculated for every plot in the Friedman–Ozawa plot, such as in Figs 3, 4 and 5, and the average value at every 5% conversion is plotted in Fig. 10 with its standard deviation. The plots are scattered, especially in the middle of the process, due to long extrapolation to the infinite temperature and the inaccuracy of the activation energy causes large error.

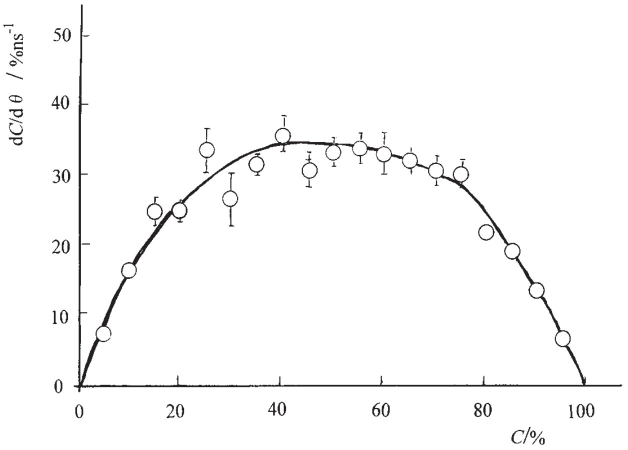

Fig. 10 Experimental master curve of reduced rate *vs*. conversion

Table 1 Estimated activation energy and reduced rate

C/%	ΔE/kJ mol^{-1}	dC/dθ/%/ns^{-1}*
5	174.1	7.5±0.5
10	154.1	16.4±0.8
15	140.9	24.7±1.9
20	155.9	24.7±1.4
25	132.5	33.8±3.4
30	143.9	26.6±4.4
35	141.0	31.5±1.1
40	141.7	35.7±3.1
45	164.9	30.6±2.2
50	157.2	33.0±2.1
55	160.6	33.8±2.5
60	171.9	32.9±3.2
65	165.4	32.2±2.2
70	164.9	30.9±2.0
75	165.4	30.5±2.0
80	157.4	24.8±0.7
85	162.6	19.2±0.7
90	159.6	13.9±0.5
95	162.4	7.0±0.5
average	156.7	–
standard deviation	2.6	–

*The unit ns is nanosecond, 10^{-9} second, and the standard deviations for the reduced rates are also tabulated

However, an arched curve obtained is a unique feature for the mechanism of random scission in the main chain or autocatalytic reaction. The former mechanism is the plausible one for the low temperature reaction of polyimide, but the theoretical curves for the random scission in the main chain [6] can not be superimposed on the experimental master curve. Considering the molecular structure of polyimide, double scissions seems to be needed to cut off the main chains, and theoretical relation for this situation has not been derived.

From these experiences we can clearly learn a new usefulness of CRTA together with advantages and reliability of the Friedman–Ozawa method over the others. In the conventional LHTG the sample is forced to be heated at a constant rate, but the temperature is adjusted following the changing reaction rate in the CRTG, so that use of both types of TG are recommended and iso-TG is also recommendable to confirm the facts. Although a set of data of the temperature, the conversion and the rate of conversion is needed for the Friedman–Ozawa method, it is the best method for kinetic analysis, as clearly seen in the above, and the set of these data can easily be obtained nowadays. Advantages of the Friedman–Ozawa method over the other are as follows [3, 4];

1. The method has the widest applicability to any type of physical properties consistent with the above-mentioned prerequisites and to any types of temperature changes.
2. The Arrhenius law is not the prerequisite.
3. It does not need approximation for calculating the reduced time, i.e., approximation of exponential integral function and zero approximation of the initial temperature of the experimental run.
4. It can be applied to diffusion processes and crystallization processes from existing nuclei [3].

Conclusions

The following are the conclusions from CRTG, LHTG and iso-TG experiments of polyimide film and their data analysis.

1. The mass loss of polyimide in air proceeds by a single step reaction in the lower temperature range below 520°C, while it proceeds by a two-step process in the higher temperature range above 550°C.
2. CRTG at low rate of mass loss observes only the low temperature reaction, while LHTG reveals both reactions but in complicated way.
3. CRTG is a very powerful and convenient tool for elucidating reaction mechanism, and it should be recommended to apply CRTG together with the conventional LHTG and iso-TG.
4. The Friedman–Ozawa method is the best method for kinetic analysis, and it can be applied to data by all types of thermal analysis, including CRTG, LHTG, iso-TG etc., so that comprehensive kinetic analysis can be made using all available data.
5. The activation energy of the low temperature reaction was estimated to be 156.7 ± 2.6 kJ mol^{-1} and the mechanism seems to be random scission in the main chain in its nature.

Simultaneous evolved gas analysis (mass-spectrometry) and thermogravimetry measurements of this material by collaboration with other researchers is now under consideration, and the results will be reported in the near future.

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