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TEMPERATURE CONTROL MODES IN THERMAL ANALYSIS

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Abstract

Now we can use several temperature control modes, i.e., the isothermal run including stepwise heating and cooling, constant rate heating (or cooling), temperature control for sample thermal history, sample controlled thermal analysis (SCTA or controlled-rate thermal analysis, CRTA), temperature jump, rate jump, temperature modulation and repeated temperature scanning. Their advantages and drawbacks are reviewed with some illustrative examples, especially for application to kinetic analysis. The combined use of these varieties of temperature control mode is recommended by showing examples. Temperature modulation and repeated temperature scanning are discussed in comparison with temperature modulated DSC, and common and analogous points are elucidated. In relation to this, the possibility that an imaginary part of overall reaction rate constant in complex reaction is postulated. Finally, these modes are classified and tabulated from two viewpoints and other possible modes are shown.

Keywords: constant rate heating, controlled-rate thermal analysis, CRTA, EGA, rate jump, repeated temperature scanning, sample controlled thermal analysis, SCTA, temperature control, temperature jump, temperature modulation, TG

Introduction

For a recent few decades, we have observed remarkable development in thermal analysis [1], especially in new techniques by which chemical and structural changes in the sample can be directly observed. Thermal analysis by Fourier transform infrared spectroscopy is one example [2]. In other examples, X-ray diffraction is observed simultaneously during differential scanning calorimetry (DSC) [3], and volatilized products are analyzed by mass-spectrometry as evolved gas analysis (EGA) together with thermogravimetry (TG) [4]. By these new microscopic techniques, we can directly observe chemical and physical changes in the sample. Thus we can learn what is going on in the sample. However, observing bulk physical property changes by classic thermal analysis, e.g., enthalpy changes by DSC, mass changes by TG and di-

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mension changes by thermodilatometry, we can only learn something is going on in the sample, but we cannot learn what is going on. Comparing the classic thermal analysis with the new microscopic thermal analysis, a great progress in thermal analysis can clearly be realized.

Another aspect of the development in thermal analysis is the diversification of temperature control modes, and nowadays we have the following modes of temperature control;

1. isothermal run, including stepwise heating and cooling
2. constant rate heating (or cooling)
3. temperature control for sample thermal history [5]
4. sample controlled thermal analysis (SCTA or controlled-rate thermal analysis: CRTA) [6]
5. temperature jump [7] and rate jump [8],
6. temperature modulation [9–11], and
7. repeated temperature scanning [12].

The last two are different in data processing. In the temperature modulated TG oscillating change of the physical property we observe is analyzed by Fourier analysis and the amplitude of the oscillating rate of conversion is compared with that of temperature modulation [11], while equivalent isothermal curves of the conversion *vs.* its rate are extracted in the latter. Details will be described below.

Each mode has its suitable applications, and the advantages and drawbacks are discussed in this paper by using illustrative applications, mainly in applications to kinetics analysis of polymer decomposition. Appropriate choice of these modes and combined use should be made. To make full use of these modes, methods for kinetic analysis are also examined, and Friedman–Ozawa plot [13, 14] is concluded to be the most suitable one because of the widest applicability. It is also postulated that an overall rate constant may have an imaginary part due to the transient change to steady state, and it would be observed as phase shift in tm-TG (or tm-DSC) and delayed change in TG (or non-modulated DSC) by repeated temperature scanning. These points are reviewed in this paper.

The third mode of temperature control is different from the other. To elucidate the nature of an observed physical transition, researchers used to observe the effect of heat treatment of the sample on the transition. One typical example is described in a reference [5], in which differential thermal analysis (DTA) was used in combination with an adiabatic calorimeter and the effect of annealing was first observed by DTA prior to the calorimetry. In another example the effect of heat treatment on polypropylene crystallization was observed [15, 16]. In this mode of temperature control, a thermal analysis instrument, such as DSC and DTA, is used as a tool for sample heat treatment to give a desired thermal history to the sample as well as a tool for observation. In TG similar heat treatment is also made within a thermobalance for instance to completely dry the sample prior to the thermal decomposition to diminish effect due to residual water [17]. Since this mode of temperature control is different from the other modes, it will not be discussed any more in this paper.

Isothermal run

The isothermal run is an old method utilized for many decades to observe reactions, and its results are very simple for us to kinetically analyze the data, but it takes a long time, when we observe reactions and their temperature dependence. This is clearly shown in one example in the next section.

However, stepwise heating and cooling, which are one of the modification of isothermal observations, are suitable for observing equilibrium as shown in an example. In Fig. 1 TG results for one of oxide superconductors are shown, $YBa_2Cu_3O_{7-\delta}$, in ambient atmosphere by stepwise heating and then cooling [18]. Final mass at each step is plotted *vs.* the temperature (Fig. 2). Because the mass observed in heating is in good agreement with that in cooling, it can be concluded that the measured mass is the mass in equilibrium and the non-stoichiometry is elucidated. This was a very important discovery, because the non-stoichiometry has much influence on the superconductivity. These results clearly illustrate the advantage of isothermal runs for observing temperature dependence

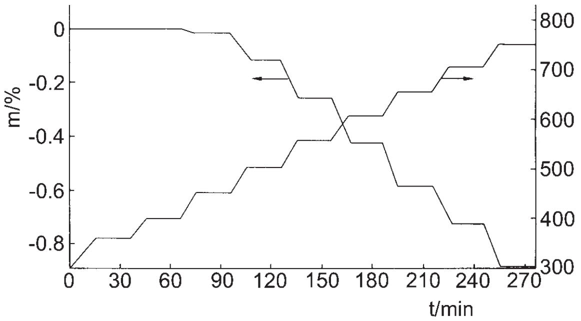

Fig. 1 TG curve of $YBa_2Cu_3O_{7-\delta}$ by stepwise heating and cooling [18]. The symbols, *m*, *T* and *t* are respectively the mass gain, the temperature and the time

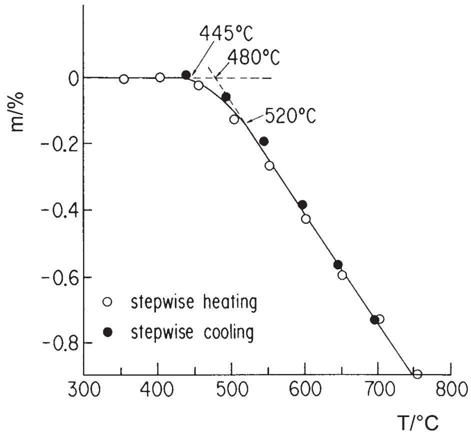

Fig. 2 Equilibrium mass change of $YBa_2Cu_3O_{7-\delta}$ observed by stepwise heating and cooling [18]

of properties in equilibrium. Similar stepwise heating was also made to obtain the relation of molten fraction with the temperature for purity determination [19].

The stepwise heating and cooling could be applied to observe the temperature dependence of steady state. Furthermore, if the change in reacting species is negligible, it can also be applied to the measurement of temperature dependence of reaction rate and hence the activation energy. This is practically used for thermal endurance evaluation of polymeric insulating materials [2].

Constant rate heating

The advantage of the observation under constant rate heating over an isothermal run can be shown by one typical example. When we observe the thermal decomposition of poly(methyl methacrylate) under high vacuum by evolved gas analysis (EGA) with a massspectrometer, we can get results shown in Fig. 3 [21]. As clearly seen in Fig. 3, volatilization by the thermal decomposition of this material proceeds as a four-step process. However, the product in each step is all monomer and other products were scarcely detected, so that the four steps of the thermal decomposition are all depolymerization, i.e., unzipping monomer from the radical end. Observing the dependence of the amount of volatilized monomer upon the initial degree of polymerization and atmosphere in the polymerization, we could conclude the following mechanism of the four step unzipping [21]. The first step unzipping starts at weak bonds, such as co-polymerized oxygen. The second and third steps are unzipping initiated at the polymer ends. There can be three types of the polymer ends, i.e., the initiator radical end, the saturated end and the unsaturated end by disproportionation in the annihilation of polymerizing radicals. But we cannot recognize which of these three types of the polymer ends are the reasons for these two unzipping processes initiated at the polymer end. The fourth and final unzipping starts by random scission in the polymer main chain. Each unzipping step is terminated with relatively short kinetic chain length by radical recombination. These are overall thermal decomposition behaviors of poly(methyl methacrylate) under high vacuum.

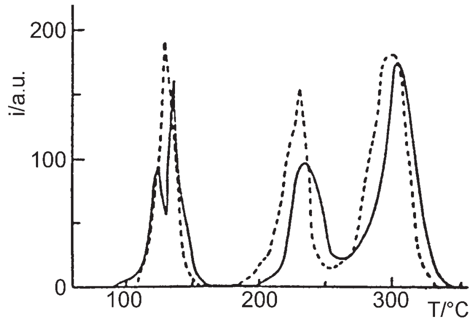

Fig. 3 EGA curves of thermal decomposition of two samples of poly(methyl methacrylate) under high vacuum [21]. The symbol, *i*, is the ion current

Imaging that we observed this process isothermally, as was done at the beginning of the polymer decomposition study, we can realize great advantages of constant rate heating over an isothermal run. When we observe it isothermally at relatively low temperature, we can observe the first-step reaction or the second-step reaction easily, but it is very hard to observe the third- and the fourth-steps, because they take a very long time and the rates of volatilization are very low. At high temperature the first and the second reactions proceed at a high rate, so that they would complete in the time interval needed to heat up the sample to a desired isothermal temperature. Therefore, if we observe this process isothermally, we need a very long time to do numerous runs, otherwise it is very hard to reach comprehensive overall understanding of the process. Although kinetic analysis of data obtained by constant rate heating is complicated [17], this example clearly shows us the advantage of constant rate heating.

Sample controlled thermal analysis

One of the advantages of constant rate heating is shown above, but its disadvantage is illustrated in the next example. When we observe the thermal decomposition of polyimide film in an ambient atmosphere by simultaneous TG-DTA at a constant rate, we get the results as shown in Fig. 4 [22]. It is clearly shown that the thermal decomposition of this material proceeds by two-step mass loss, and when we see the DTA curve, it is much more clear, because we can see two exothermic peaks. Even if we change the rate of heating, the nature of the two-step decomposition essentially does not change. However, when we observe the same decomposition process in the same atmosphere by SCTA, namely sample controlled TG (SCTG or CRTG), the results we obtained are quite different, as shown in Fig. 5 [22]. Because the temperature changes smoothly and does not change discontinuously to keep a constant mass loss rate, we can conclude that the decomposition proceeds by a single step process.

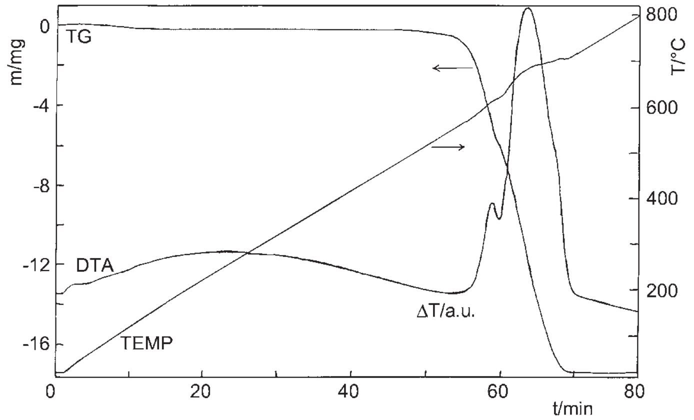

Fig. 4 TG–DTA curve of thermal decomposition of polyimide film in air flow by constant rate heating at 10°C min^{-1} [22]. The temperature difference ΔT by DTA is shown in an arbitrary unit

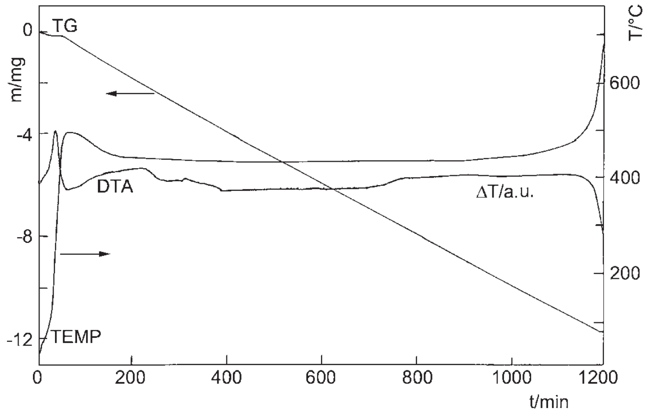

Fig. 5 SCTG curve of polyimide film in air flow obtained at mass loss rate of 0.06% min^{-1} [22]. The temperature difference by DTA is also shown

To examine these contradictory results, kinetic analysis was applied to both data by constant rate heating and by SCTG. For this purpose Friedman–Ozawa plot [13, 14] is only a reliable iso-conversion method for estimating the activation energy, because this plot can be applied to data obtained by any temperature change. In the other iso-conversion methods, i.e., Ozawa–Flynn–Wall plot [17, 23] and Kissinger–Akahira–Sunose plot [24, 25], however, the constant rate heating is one of the pre-requisites. Therefore, they cannot be applied to data by the other temperature

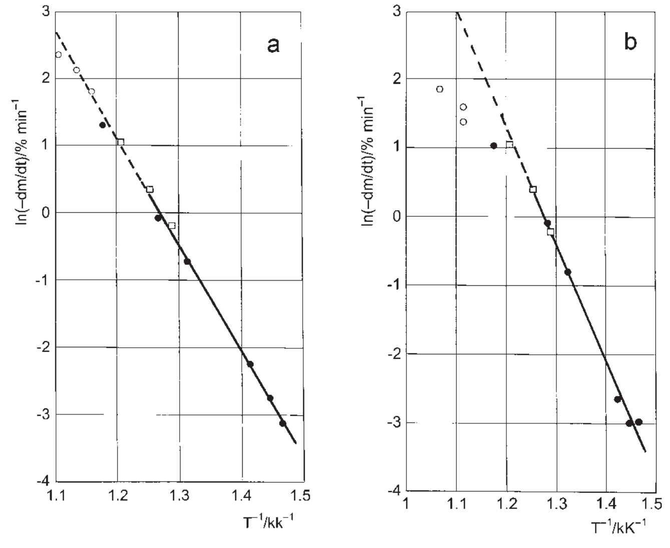

Fig. 6 Friedman–Ozawa plot for thermal decomposition of polyimide film [22]. The symbols, o, • and □, are respectively data by constant rate heating, SCTG and isothermal run. Mass loss conversion of 25% (a) and 35% (b)

control modes. The results are shown in Figs 6a and b, in which data obtained by isothermal runs are also plotted. Linear plots are obtained for data in a temperature range below about 500°C, but data above this temperature tend to deviate from the linear plots. Thus, this fact suggests that the decomposition mechanism changes in this temperature range.

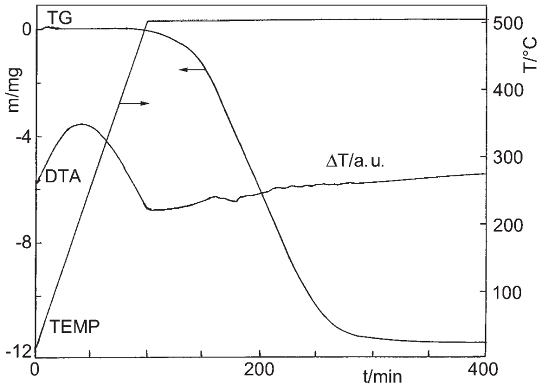

Fig. 7a Isothermal TG-DTA curves of polyimide film in air flow obtained at 500°C [22]

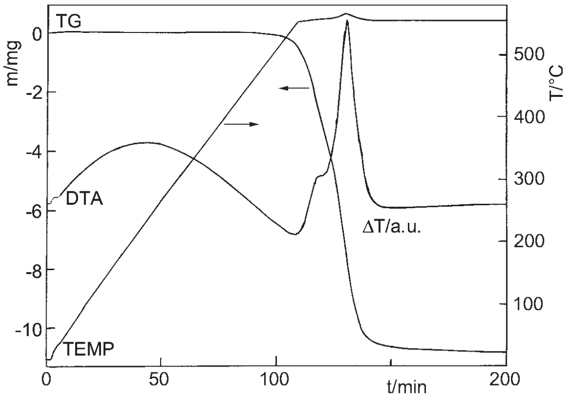

Fig. 7b Isothermal TG-DTA curves of polyimide film in air flow obtained at 550°C [22]

To confirm this speculation, isothermal observations were carried out in this temperature range, and the results are reproduced in Fig. 7. It was confirmed that the thermal decomposition below 500°C proceeds by a single step (Fig. 7a), while it is a two-step process above 550°C (Fig. 7b). By observing this process by SCTG at a higher mass loss rate, we can observe two-step decomposition in a higher temperature range.

The thermal decomposition behavior of this material is, thus, shown schematically in Fig. 8 [22]. Two reaction processes are competing. One is the single-step mass loss and predominant in a low temperature range. The other is the two-step mass

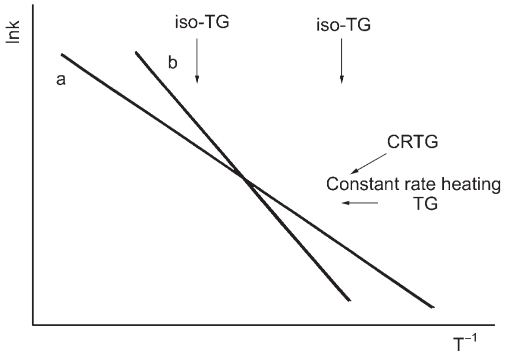

Fig. 8 Schematic expression for temperature dependence of reaction rate constants, *k*, for two competing reactions [22]

loss and predominant in a high temperature range. By the isothermal run we observe either of these two processes, as shown with arrows in the figure. By constant rate heating we observe both; first the low-temperature predominant process is observed but later the high-temperature process becomes predominant, as the temperature increases. When we observe the decomposition by controlling the mass loss rate at relatively low rate by SCTG, we can mainly see the low-temperature predominant process. However, when we observe it at high rate of mass loss by SCTG, the high-temperature predominant process is observable. Thus, what we see by thermal analysis is changed by temperature control mode we applied.

The usefulness of SCTA has been clearly elucidated for consecutive reactions of inorganic substances, especially for stepwise dehydration of crystalline water, and it is also shown for organic substances in differentiated evaporation of crystalline water from free water. Thus high resolution of SCTA has been well recognized. However,

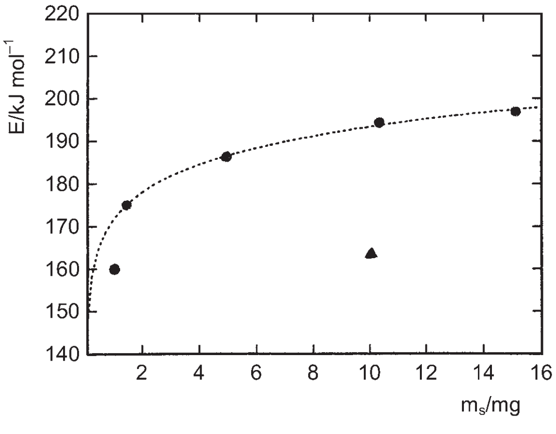

Fig. 9 Sample mass (m_s) dependence of activation energy (E) obtained by TG of poly(butylene terephthalate) [26]. The symbols, • and ▲, are respectively data by constant rate TG and SCTG

another usefulness of SCTA is shown above, and in this application an advantage of SCTA was revealed that the reaction proceeds at a constant desired rate in an automatically searched appropriate temperature range. Thus, this illustration also suggests us that we can investigate real thermal behavior only by combined use of various temperature control modes.

Another advantage of SCTG was postulated for polymer decomposition [26]. When thermal decomposition of poly(butylene terephthalate) under nitrogen flow was observed by constant rate heating modes and the activation energy was estimated by the Ozawa–Flynn–Wall plot, the estimated activation energy is dependent apparently on the sample mass [27]. However, when it was observed at various constant mass loss rates by SCTG and the data were analyzed by Friedman–Ozawa plot, the activation energy estimated for a large sample mass is in good agreement with that estimated for a small mass sample by constant rate heating (Fig. 9) [26]. Thus it seemed that the apparent sample mass effect was not detected in SCTG results. Because the mass loss rate is controlled at a given rate in SCTG, volatilization of the products and hence the product partial pressure above the sample are also roughly controlled, and this controlled atmosphere seems to be a cause for the activation energy independent on the sample mass.

Kinetic analysis methods

It seems worth discussing the kinetic analysis methods in relation to the temperature control modes. It has been recognized that iso-conversion methods, such as the Ozawa–Flynn–Wall plot [17, 23], the Kissinger–Akahira–Sunose plot [24, 25] and the Friedman–Ozawa plot [13, 14], are the most reliable methods for estimating the activation energy using thermoanalytical data [28], because these three plots are all so-called ‘model-free’ plots.

As clearly seen in the above, however, the Friedman–Ozawa plot has advantages over the Ozawa–Flynn–Wall plot and the Kissinger–Akahira–Sunose plot. In other words, the Friedman–Ozawa plot is a single method that is applicable to data obtained by the combined use of various temperature control modes. Because the combined use of different temperature control modes is a powerful mean to get overall thermal decomposition behavior, this point is very important for kinetic investigation of materials, especially organic materials.

When these three plots were devised, a computer was not installed with a thermal analysis instrument, so it is hard to get the rate of conversion for an integral type thermal analysis, such as TG. At the same time, constant rate heating was mainly used for almost all thermal analysis. Under these historical circumstances, the three plots were proposed, and the Ozawa–Flynn–Wall plot and the Kissinger–Akahira–Sunose plot have been widely applied to data by constant rate heating, because it needs only the conversion and the temperature not the rate of conversion. Friedman proposed his plot in 1964 [13], but it was not so easily applicable, because the rate of conversion is needed. Furthermore, Friedman applied his plot only to *n*-th order reaction, so the applicability of his initial plot was thought to be limited. Later the present author found it applicable to other processes as widely as the other two plots (Expanded Friedman plot or Friedman–Ozawa plot) [14]. As computerization was promoted, the situation has changed and Friedman–Ozawa plot has become an easily applicable and reliable plot for estimating the activation energy. The other two are reliable, but they have a historical limit, because their applicability is limited.

It should also be noted that the reduced time or the generalized time is very useful to learn the mechanism function of the process by deriving experimental master curves using the generalized time or the reduced time [17, 29, 30]. In a course of this derivation, we can also examine the applicability of the method to the process under investigation [17, 29]. The concept of the reduced time is independently applied to all data by any temperature control modes, though the calculation of the reduced time for constant rate heating is not so difficult as for other modes.

Temperature jump and rate jump

These jump methods were devised to estimate the activation energy. As is illustrated in Fig. 10, when we abruptly change the temperature as shown in the bottom, this jump in the temperature is reflected in a corresponding jump in the rate constant, and hence it appears as a jump in the conversion rate we are observing [7]. In reverse, when we abruptly change the conversion rate in SCTA, it is reflected in the temperature jump [8]. Therefore, we can compare the rate constants at the two temperatures at the rate jump or the temperature jump, because the rate is proportional to the rate constant at the jump, namely at a given conversion. This is based on the same principle

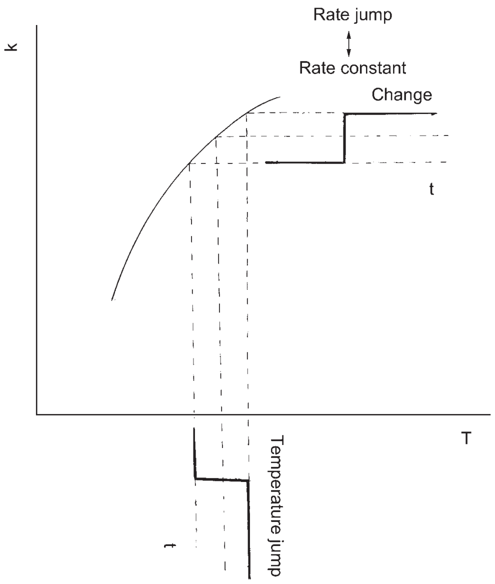

Fig. 10 Schematic explanation of jump methods

with Friedman–Ozawa plot, so it is widely applicable. These jump methods, therefore, is the most direct method to estimate the activation energy. In practical experiments, the temperature and the conversion rate do not change so abruptly as in the figure due to the thermal response of the system, and the rate or the temperature extrapolated to the given conversion at the jump is used for the evaluation of the activation energy.

These jump methods seem to be useful for kinetic analysis of parallel competitive reactions. For these reactions a method is proposed and in this method the volatilization rates of products by each competing reaction are measured and compared with each other at a given amount of residual reacting species [31]. This is also an expansion of Friedman–Ozawa plot. However, one of the difficulties of this method is to specify the point of the given amount of residual reacting species for different runs, if we do not have a tool for direct measurement of the amount of residual reacting species. Otherwise, we should know exact chemical stoichiometry of all products, because the relative amount of each product is dependent on the path or the trajectory of the process [32], and thus we can estimate the amount of residual reacting species from the amount of all volatilized products. By the jumps in the temperature or the rate of a certain volatile product, on the other hand, we can compare the volatilization rates of products by each competing reaction at a given amount of residual reacting species at different temperatures. Therefore, we can observe difference in the temperature dependence of the rate constant among the competing reactions, and it is the first step to elucidate the mechanism. A similar advantage of the jump methods seems to be expected also for consecutive reactions.

Temperature modulation

Temperature modulation was first introduced into thermal analysis as temperature modulated DSC [9, 10], and since its publication in 1992 various researches have been done to investigate complex response of the sample under temperature modulation. In this course of progress, temperature modulation was applied to other techniques, and temperature modulated TG (tm-TG) was proposed [11]. The sinusoidal temperature modulation causes oscillation of the rate constant and hence oscillation of the rate of mass change, as illustrated in Fig. 11.

In tm-TG the oscillating rate of mass loss by the temperature modulation is observed together with mass loss. In some cases the temperature modulation is superimposed on the underlying constant rate heating, and in other cases of quasi-isothermal measurement the temperature is modulated around the underlying constant temperature. One of examples of tm-TG curves is reproduced in Fig. 12 [11]. In both ways of tm-TG the amplitude of the oscillating rate of mass loss is compared with the amplitude of temperature modulation and the activation energy is estimated in real time by this comparison.

There are a few points to be noted [12]. The first is the non-linear dependence of the rate constant on the temperature. Due to this non-linearity, the sinusoidal temperature modulation is non-linearly reflected in the oscillating rate, and the rate oscilla-

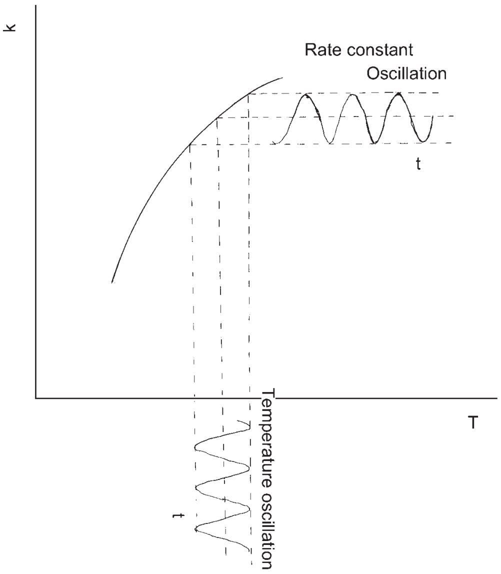

Fig. 11 Schematic explanation of temperature modulation method

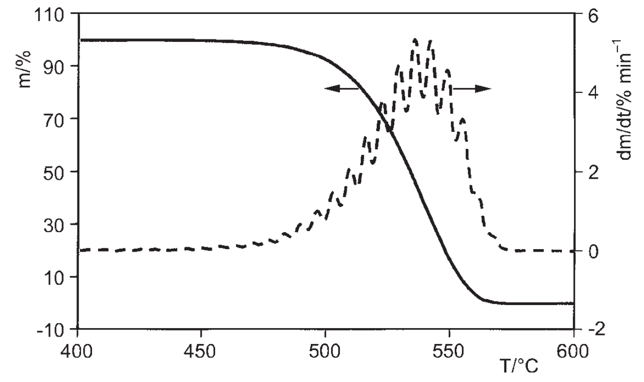

Fig. 12 Temperature modulated TG curve of polytetrafluoroethylene [11]

tion becomes deformed. In the other word, accelerating effect in the temperature range above the average temperature is lower than the decelerating effect in the lower temperature range, so the change in the rate constant becomes different from the sinusoidal change. Because the amplitude of the rate oscillation is calculated by Fourier analysis based on the linearity, the linearity is one of prerequisites for this method to estimate the activation energy. Therefore, the essential non-linear effect should be negligible, so that the amplitude of the temperature modulation should be low, for instance less than ±10°C, but it depends on the temperature and the activation energy.

As mentioned above, the temperature modulation has been applied to various thermal analyses. Although it has not yet been applied to EGA, it would become a useful and interesting technique especially for parallel competitive reactions because of the above reasons. By comparing the amplitudes of oscillating volatilization rates of various products, we could learn the difference in the activation energy and the number of involved reactions.

Repeated temperature scanning

This temperature control mode is similar to the temperature modulation but different in the kinetic method [12]. In this temperature control mode, the sample is repeatedly heated and cooled in a desired and defined temperature range, and the triangular saw-teeth modulation is preferable to the other modulations, because the reduced time can easily be calculated for this modulation. Because the rate of conversion is the same at a given conversion and a given temperature in any temperature control modes, the relation between the rate of conversion and the conversion can be extracted at a given temperature from data obtained by this temperature mode. This relation is an equivalent isothermal curve of the rate of conversion *vs.* the conversion and it is equal to that obtained by the isothermal run. When we make similar extraction at different temperatures, we can get equivalent isothermal curves at multiple different temperatures. Thus it is the essence of the method that data by repeated temperature scanning are transformed to multiple equivalent isothermal curves.

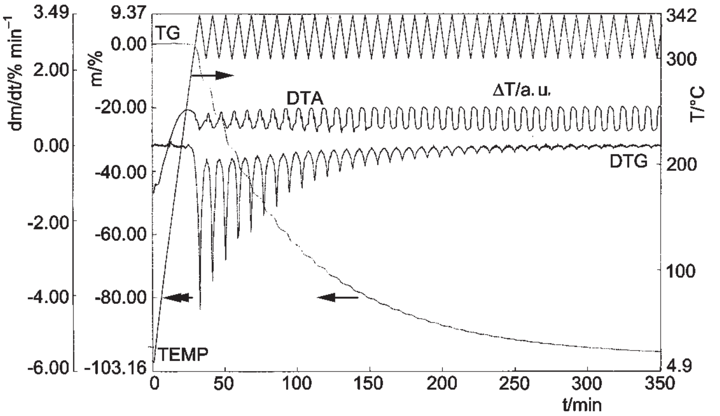

Fig. 13 TG – DTA curve of poly(methyl methacrylate) by repeated temperature scanning

This method was applied to the thermal decomposition of poly(methyl methacrylate) of high molecular mass and poly(butylene terephthalate) in nitrogen flow [33]. A typical result is shown in Fig. 13. By extracting the conversion and the rate of conversion at given temperatures, we get multiple equivalent isothermal curves for poly(methyl methacrylate) and they are reproduced in Fig. 14. As described above this material undergoes unzipping and it is a first-order reaction, which is clearly seen

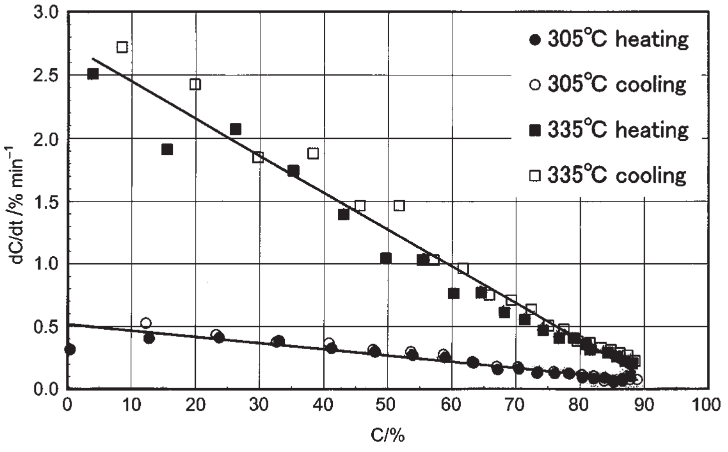

Fig. 14 Equivalent isothermal curves of conversion (*C*) *vs.* conversion rate extracted from TG curve of poly(methyl methacrylate) in Fig. 13

in linear relations in Fig. 14. A slight difference was observed between the data obtained in the heating mode and those in the cooling mode. This is discussed below. Thus usefulness of this temperature control mode is clearly shown, and it is also very clear that it is time-saving.

For poly(butylene terephthalate) equivalent isothermal curves are shown in Fig. 15. As is seen in this figure, we got the two curves for one temperature; the curves obtained in the heating mode are different from those in the cooling mode, though the arched form of curves is typical of random scission in the main chain of this polymer [26, 27]. One of the plausible causes for this discrepancy seems to be temperature lag. The recorded temperature is not the sample temperature but the tem-

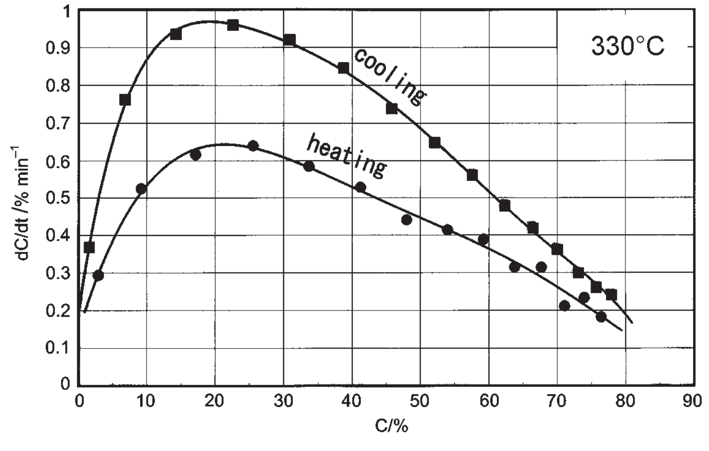

Fig. 15 Equivalent isothermal curves of conversion rate *vs.* conversion for poly(butylene terephthalate) at 330°C

perature of the temperature sensor (the thermocouple), and there is temperature gradient around the sample for heat flow. In this particular case in Fig. 15, the sample temperature changed with some lag from the recorded temperature, so the sample temperature is lower by a certain degree than the recorded temperature in the heating mode and higher in the cooling mode. This effect is schematically shown in Fig. 16. It also exists in any temperature change, including the constant rate heating, but until now the reaction is usually not observed by the cooling mode nor compared with heating mode, so this effect has not yet been noticed. It is also clearly shown that the temperature measured by TG should be corrected by using standard materials, such as magnetic standards [34]. The temperature difference between the heating mode and the cooling mode was also detected by using the magnetic standards [34].

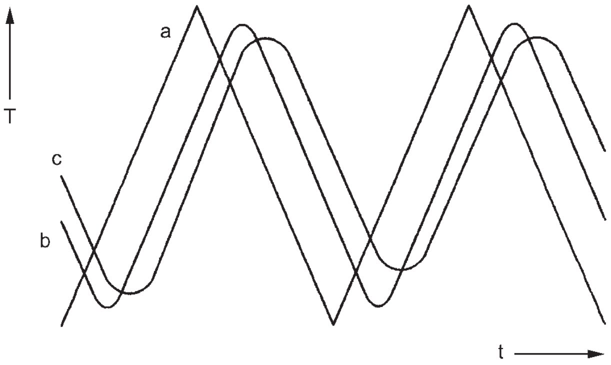

Fig. 16 Schematic drawing of a – recorded temperature, b – sample temperature and c – rate change

This temperature lag seems to be existing in tm-TG as phase shift in the mass loss rate, though it has not yet been reported, and this is also existing in tm-DSC [35]. Furthermore, this effect is common in the technique by temperature modulation. When the modulated temperature wave is propagating in the instrument and in the sample by thermal conduction, always the amplitude is decreased and the phase is shifted, and thermal contacts among the sample, the cell and the cell holder plate are other reasons for this effect. The higher the frequency is, the larger the effect is. Therefore, there are the same and common problems between the repeated temperature scanning and the temperature modulation. The heat of reaction also disturbs the temperature control.

However, there might be another cause of the above discrepancy, and it is the transient change to the steady state. One possible example is unzipping the monomer from the radical ends [21, 36]. As described above, this process proceeds as a first-order reaction in a steady state in which the radical concentration is kept at a constant concentration, because the rate of annihilation of the radical by recombination becomes equal to that of the radical formation by chain scission. The rate of unzipping is proportional to this constant radical concentration, and this concentration is dependent on the temperature mainly because of the activation energy of the radical formation. In the repeated temperature scanning the radical concentration changes as the temperature changes. If there is a certain lag in this change of the radical concentration, it becomes a reason for the delay in the change in the rate of unzipping. Thus, there is a possibility that transient change to the isothermal rate might be detected as the delay in the temperature change of the rate in the heating and cooling mode, and it is also detected in retarded change of the rate in the temperature jump. In tm-TG it appears as the phase lag and the amplitude decrement. Thus there might be imaginary part in overall rate constant of complex reactions.

This is analogous to the imaginary part of heat capacity [35]. However, the imaginary part of heat capacity is caused by relaxation to the equilibrium, but the imaginary part of overall rate constant is different from the relaxation but the transient change to the steady state in the complex reaction. Both of these imaginary parts cause the decrease in the amplitude and the shift in the phase (or the delay in the rate change in the repeated temperature scanning and in the jump methods). Therefore, these changes are observed together with the similar effect by the temperature wave propagation (or the temperature lag), so a problem to be solved is to separate apparent effect by these instrumental and procedural causes from the imaginary part which seems to be really existing. This is also a common problem between the repeated temperature scanning and the temperature modulation and also between tm-DSC and tm-TG.

Classification and other modes of temperature control

The temperature control modes described above can be classified from two viewpoints, i.e., the underlying control and the superposed control, and it is shown in Table 1. From this classification other possible temperature control modes are revealed, as shown in the table, but some of them are not yet named properly.

Table 1 Classification of temperature control modes

		Superposed control		
		No superposition	Modulation	Repeated scanning
Underlying Control	Constant temperature	Isothermal run	Quasi-isothermal	Repeated temperature scanning
			Temperature modulation	
	Constant rate heating (Linear heating)	Constant rate heating (Linear heating)	Linear heating temperature modulation	Not named
	Sample controlled (Constant rate)	SCTA (CRTA)	Rate modulation	Repeated rate scanning

The underlying control modes have common characteristics, which are independent upon the superposed control modes. In the case of constant rate heating, the process can easily be observed up to its final stage by accelerating effect of temperature increase. Similarly we can also observe the final stage by the SCTA mode within the estimated time, because the rate of conversion is controlled. On the other hand, by the isothermal run the conversion rate decreases and finally it becomes so low that it cannot be measured because of low signal/noise ratio and we can hardly observe the change in the conversion per se.

The superposed control modes have also common characteristics. By the modes of the temperature jump, the rate jump, the temperature modulation and the rate modulation, the activation energy is estimated easily by comparing the temperature jump *vs.* the rate jump or the temperature amplitude *vs.* the rate amplitude. However, they are not so suitable for elucidating the mechanism function as the others, and the amplitudes should not be so large, as mentioned above. In the temperature scanning mode and the rate scanning mode, the equivalent isothermal relations between the conversion and the conversion rate are directly extracted, so the mechanism function can be easily elucidated.

Conclusions

1. Advantages and drawbacks of various temperature control modes are shown with some examples of application.
2. Choice of these modes is required to make appropriate thermal analysis.
3. Furthermore, combined use of these modes is recommended to elucidate the whole thermal behavior of the sample, and it is especially important for organic substances, such as polymers, because the reaction mechanism might change by the temperature change.
4. It was found by repeated temperature scanning that thermal decomposition observed in cooling mode tends to differ from that observed in heating modes. It is caused by the difference between the recorded temperature and the sample temperature due to thermal gradient around the sample for heat flow.
5. However, there may be another cause, i.e., lag in rate for instance due to transient change to the steady state, which is also changing by the temperature change.
6. They would be observed as amplitude decrement and phase angle shift in tm-TG.
7. These phenomena are common and analogous to those in tm-DSC.
8. The various temperature control modes can be classified by the two viewpoints, i.e., the underlying control and the superposed control. Their characteristics or their advantages and drawbacks are described from these points of view.

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