

A MODIFIED METHOD FOR KINETIC ANALYSIS OF THERMOANALYTICAL DATA

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A method is devised by modification of the author's previous method. Thermo-analytical data are transformed to equivalent isothermal ones, and linear relations are utilized to elucidate the mechanism and the pre-exponential factor, instead of curve-fitting. Advantages are illustrated by applying this method to the decomposition of polycaprolactam.

Previously, the author proposed a method for kinetic analysis of thermoanalytical data [1, 2]; in this method the activation energy is estimated first by utilizing the linear relation between the logarithm of the heating rate and the reciprocal absolute temperature at a given conversion or at the peak of the derivative thermo-analytical curve, and then, in order to elucidate the reaction mechanism and the pre-exponential factor, experimental master curves between the reduced time [1], the conversion and the reduced rate of conversion [2] are drawn and compared with corresponding theoretical curves by curve-fitting. This method has been applied to the decomposition of polymethylmethacrylate [3], the volatilization of impurities from an epoxy resin [4] and so on, and has further been extended for application to diffusion [5].

However, the method of curve-fitting is not convenient in general as it is neither easy nor plain to judge which of the theoretical relations is fitted best to the curve derived from the experimental data, especially when minor reactions occur concurrently. Utilization of linear relations is preferable to curve-fitting for this purpose. For instance, there is a slight difference between the theoretical integral curve of the first-order reaction and those of random scissions in the main chains of polymer, so that discrimination between them by the integral type of thermal analyses, such as thermogravimetry, is difficult using the curve-fitting method. Furthermore, when there is a minor reaction and the chemical structural change due to the minor reactions becomes appreciable in the later stage of the process, the difficulty in the curve-fitting becomes serious and there is then a great advantage in utilizing linear relations. In this report, a method modified by utilizing linear relations is devised, and is applied to the decomposition of polycaprolactam in vacuo. Advantages of the new method are pointed out and discussed.

The modified method

Activation energy can be estimated by plotting the logarithm of the heating rate against the reciprocal absolute temperature at a given conversion or at the peak of the derivative thermoanalytical curve. This method of estimating the activation energy is generally applicable to all types of phenomena which are governed by a single activation energy, and is easily applied. As described previously [1, 2], we can transform the integral thermoanalytical data to the experimental master curve by introducing the reduced time, Θ :

$$\Theta = \int \exp\left(-\frac{\Delta E}{RT}\right) dt \quad (1)$$

where ΔE , R , t and T are the activation energy, the gas constant, the time and the temperature as a function of the time, respectively, i.e., the reduced time can be calculated by using an estimated ΔE and p -function [6] at a certain temperature and a heating rate, a , because

$$\Theta = \frac{\Delta E}{aR} p\left(\frac{\Delta E}{RT}\right) \quad (2)$$

and

$$p(y) = \frac{\exp(-y)}{y} - Ei(-y) \quad (3)$$

where $Ei(-y)$ is the exponential integral function. The derivative thermoanalytical curve can also be transformed to the similar experimental master curve, because

$$\frac{dC}{dt} = \frac{dC}{d\Theta} \exp\left(\frac{\Delta E}{RT}\right) \quad (4)$$

The experimental master curve between the conversion and the reduced time, and that between the reduced rate of conversion, $dC/d\theta$, and the reduced time or the conversion are both equivalent to the relations in isothermal experiments, because the reduced time is proportional to the actual time in the isothermal experiment and is the actual time when the process proceeds at infinitely high temperature. Thus, the transformation of the thermoanalytical data to the experimental master curves is equivalent to transformation to the equivalent isothermal data. Therefore, the thermoanalytical data can be analyzed in a way similar to that for the isothermal kinetic data by transformation to the equivalent isothermal data. For example, if the reaction under consideration is a first-order one, $-\ln(1 - C)$ is proportional to the reduced time and the pre-exponential factor can be estimated from the slope of the linear plot. For the integral thermoanalytical curve, the quantity listed in the second column of Table 1 is proportional to the reduced time, and when it is plotted on the ordinate and the reduced time on the abscissa for an assumed mechanism straight line is obtained if the assump-

tion is correct, its slope being equal to the pre-exponential factor. For the derivative thermoanalytical curve, the quantities listed in the third column of Table 1 should be plotted against the reduced rate, and the slope is the pre-exponential factor.

Table 1
Quantities proportional to the reduced time or reduced rate of conversion

Mechanism	Quantities proportional to the reduced time	Quantities proportional to the reduced rate
First-order reaction	$-\ln(1 - C)$	$(1 - C)$
n -th order reaction ($n \neq 1$)	$[(1 - C)^{1-n} - 1]/(n - 1)$	$(1 - C)^n$
Random scission	$-\ln(1 - x)$	$(1 - x)$
Diffusion-controlled reaction	C^2	$1/2C$

An example of the application of the modified method

The modified method described above is applied to the TG curves of the decomposition of polycaprolactam in vacuo; the experimental data and the experimental master curve obtained were described elsewhere [1]. If the process is random

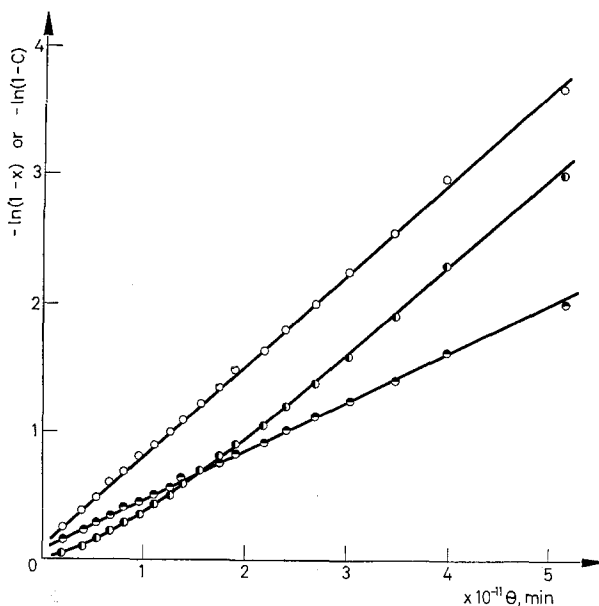


Fig. 1. Plots of $-\ln(1 - x)$ and $-\ln(1 - C)$ against the reduced time. The ordinate for \circ is $-\ln(1 - x)$ on the assumption of a least degree of polymerization of two, that for \circ is $-\ln(1 - x)$ on the assumption of a degree of three, and that for \bullet is $-\ln(1 - C)$ on the assumption of a first-order reaction

scission in the main chains of the polymer, the logarithm of the fraction of unbroken bonds, $\ln(1 - x)$, varies linearly with the reduced time, where x is the fraction of bonds broken and can be calculated from the conversion for an assumed value of the least degree of polymerization of unvolatilized polymer [1, 2], while the logarithm of $(1 - C)$ varies linearly with the reduced time if the process is a first-order reaction. In Fig. 1, both quantities are plotted against the reduced time. Since the logarithm of $(1 - x)$ is a linear function of the reduced time, the process is random scission in the main chains of the polymer. However, both plots in which the least degree of polymerization of unvolatilized polymer is assumed to be either two or three vary linearly with the reduced time, though the regression lines do not pass through the origin in either case, and the least degree of polymerization of unvolatilized polymer can not be estimated exactly; uncertainty in the value seems to be natural, taking into account the small difference in the theoretical curves in the two cases. However, deviation around the regression line is smaller in the case of a least degree of two than in the case of three, so that the estimated value of the least degree of polymerization of unvolatilized polymer is two; this result is consistent with result obtained by the previous curve-fitting method [1]. The pre-exponential factor estimated from the slope in Fig. 1 is $7.0 \times 10^{10} \text{ min}^{-1}$ and that obtained by the previous method is $8.1 \times 10^{10} \text{ min}^{-1}$; this agreement is reasonably good.

Discussion

Methods for kinetic analysis of isothermal data are well established and are plain and easy, while the kinetic analysis of thermoanalytical data is complicated. However, isothermal experiments can often not be made; for instance, when it takes a relatively long time compared to the reaction rate to heat the reaction system up to a desired temperature, the reaction proceeds to some extent during the heating-up period and kinetic analysis of the reaction often becomes almost impossible. Therefore, thermoanalytical experiments must be made, though kinetic analysis is complicated and sometimes leads to false and unreal results due to inappropriate methods [7]. However, by the transformation of the thermoanalytical data to the equivalent isothermal ones by using the reduced time, we can eliminate the difficulties mentioned above, and apply the well-established methods for isothermal data to the transformed non-isothermal data of thermal analyses.

We obtain another advantage from this transformation, i.e., we can utilize linear reactions of isothermal kinetics to elucidate the reaction mechanism and to estimate the pre-exponential factor. This advantage is decisive in discrimination between the first-order reaction and random scission in the main chains of the polymer for the integral thermoanalytical data, as is demonstrated above. On the other hand, there is a clear difference between the transformed derivative curves of these reactions; there is a maximum in the transformed master curve of the reduced rate vs. the conversion for the random scission, but there is no maximum for the n -th order reactions [8].

Another advantage may be gained when minor reactions exist. In this case, some deviations from the linear relation may be found in the later stages of the process, because the minor reactions change the chemical structure gradually; in the later stages this accumulates to such an extent that deviations can be detected. This effect may also be detected in scattering in the experimental master curve, as observed in the thermal decomposition of polyethylene terephthalate in vacuo [9].

In conclusion, the previous curve-fitting method is suitable for preliminary elucidation of the mechanism, while the method utilizing the linear relations proposed in this report is that preferred for exact and detailed examination of the data.

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RÉSUMÉ — La méthode précédemment proposée par l'auteur est modifiée. La nouvelle méthode qui est présentée transforme les données thermoanalytiques en données isothermes équivalentes et utilise des relations linéaires pour établir le mécanisme et le facteur pré-exponentiel au lieu de la méthode antérieure avec ajustement des courbes. Les avantages de cette nouvelle méthode sont illustrés en l'appliquant à la décomposition du polycaprolactane.

ZUSAMMENFASSUNG — Es wurde eine neue Methode durch Modifizierung der früheren Methode des Autors entwickelt. Bei der neuen Methode werden die thermoanalytischen Daten in isotherme umgewandelt und anstatt der Kurven-Anpassung der vorhergehenden Methode werden lineare Zusammenhänge zur Klärung des Mechanismus und des pre-exponentiellen Faktors eingesetzt. Die Vorteile der neuen Methode werden durch ihre Anwendung bei der Untersuchung der Zersetzung von Polycaprolactan veranschaulicht.

Резюме — Путем усовершенствования собственного метода, авторами разработан новый метод, в котором термоаналитические данные превращаются в эквивалентные изотермические и используются линейные соотношения для того, чтобы объяснить механизм и предэкспоненциальный фактор, вместо сглаживания кривой, как это было предложено в предыдущем методе. На примере разложения поликапролактама показаны преимущества нового метода.