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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

A SIMPLE METHOD FOR ESTIMATING ACTIVATION ENERGY FROM DERIVATIVE THERMOANALYTICAL CURVES AND ITS APPLICATION TO THERMAL SHRINKAGE OF POLYCARBONAYE

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Activation energy can be estimated by a new simple method, in which logarithm of maximum rate of conversion observed at different heating rates is plotted against reciprocal absolute temperature, because the conversion at the maximum rate is approximately independent of the heating rate. The method is applied to thermal shrinkage of polycarbonate, and the estimated activation energy is in good agreement with those obtained by conventional methods.

For estimating activation energy from thermoanalytical curves, numerous methods have been proposed. Most of them are based on particular kinetic equations, and their applicability is, therefore, limited, because they can not be applied to processes other than those following the particular kinetic equations. When the methods are applied to these processes, they tend to lead false and wrong kinetic parameters and mechanism.

A few methods, such as proposed by Flynn and Wall [1], Friedman [2, 3] and one of the present authors [3–7], were derived from a general form of the kinetic equation and their applicability is not limited to particular kinetic models, but they have wide applicability to processes of single elementary process following Arrhenius type temperature dependence of activation energy. One example is application to physical processes, such as

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thermal shrinkage [8]. However, there are two methods for estimating activation energy from derivative thermoanalytival curves, such as evolved gas analysis (EGA) curves [5–7, 9].

In one method, logarithm of the heating rate is plotted against reciprocal absolute temperature at the maximum rate of conversion obtained at different rates of linear heating, and the activation energy can be estimated from the slope of this linear plot. This method is based on a principle that the linear relation, which is obtained for linear heating thermal analysis results obtained at different heating rates, hold at a given conversion and the slope of the linear plot is proportional to the activation energy and independent from the other variables [1, 4, 6, 7], while the conversion at the maximum rate of conversion is the same and independent on the heating rate [5–7].

In the other method [5, 9], logarithm of the heating rate deivided by the square of the absolute temperature is plotted against the reciprocal absolute temperature, and the activation energy is similarly estimated.

For estimating the activation energy, another linear relation can be derived for the results by linear heating thermal analysis by utilizing the above independence of the conversion at the maximum rate, and it is described in this paper. The proposed method has been applied to thermal shrinkage of a polycarbonate at different heating rates, and the activation energy estimated by the method is in good agreement with those obtained by conventional methods. These results are also reported in this paper.

Theoretical consideration

To begin with, two general equations are shown below, because these two are prerequisits for the new method [10].

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

where C and x are conversion of the physical properties we observe in the thermal analysis and the conversion of the structural quantity which changes during heating, respectively, and $F(x)$ means a general single-valued function of x. The second general equation is as follows;

$$x = G(\theta) \tag{2}$$

and θ is generalized time [10] and $G(\theta)$ means a function of the generalized time. The generalized time is given below:

$$\theta = \int \exp\left(-\frac{\Delta E}{R\,T}\right) \mathrm{d}t \tag{3}$$

where ΔE, R, T and t are the activation energy, the gas constant, the absolute temperature and the time, respectively. The second prerequisite, i.e., Eq. (2), holds for various processes, in which the rate constant follows Arrhenuis law.

One example is usual chemical reaction, in which single elementary reaction proceeds [4, 5];

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A \exp\left(-\frac{\Delta E}{R\,T}\right) g(x) \tag{4}$$

where A is the pre-exponential factor, and $g(x)$ means another single-valued function of x, such as $(1\text{-}x)^n$.

Another example is diffusion in which the diffusion constant follows Arrhenius law [5];

$$\frac{\partial x}{\partial t} = D_0 \exp\left(-\frac{\Delta E}{R\,T}\right) \nabla^2 x \tag{5}$$

where $Do \exp(-\Delta E/RT)$ and x are the diffusion constant and the concentration of diffusing species, respectively, and ∇^2 is a Laplacian operator.

The growth from pre-existing nuclei is also the case [7];

$$-\ln(1\text{-}x) = Z\,\theta^m \tag{6}$$

where $Z \exp(-\Delta E/RT)$ is the growth rate and m is the growth dimension.

At the maximum rate of conversion the next equation holds;

$$\frac{\mathrm{d}^2 C}{\mathrm{d}t^2} = 0 \tag{7}$$

Substituting Eqs (1), (2) and (3) into Eq. (7) and taking accounts of heating at a constant rate (this is the third prerequisite) we obtain [5–7]

$$\theta \frac{\mathrm{d}^2 C(\theta)}{\mathrm{d}\theta^2} + \frac{\mathrm{d}C(\theta)}{\mathrm{d}\theta} = 0 \tag{8}$$

where an approximation, i.e., $\exp(-\Delta E/RT)\,\mathrm{d}t = RT^2 \exp(-\Delta E/RT)/E^2\,\varphi$ is applied for the heating rate of φ [11]. In Eq. (8) the heating rate is not included, and $C(\theta)$ and θ are only the variable involved. Therefore, at the maximum rate of conversion, the generalized time, θ, is the same and independent from the heating rate. Thus C and x become also the same, because of the Eqs (1) and (2).

Therefore dx/d is proportional to the rate constant at the maximum rate of conversion [2, 3]. Because

$$\frac{dC}{dt}=\frac{dC}{dx}\frac{dx}{dt} \tag{9}$$

and dC/dx is a constant at the same conversion, x, dC/dt is proportional to the rate constant. Thus, when logarithm of dC/dt (not dC/dT), i.e., the height of the peak from the base line in the derivative thermoanalytical curve, is plotted against the reciprocal absolute temperature at the peak, the linear plot can be obtained and this is an Arrhenius plot and also an extension of Friedman plot [2, 3], if the above three requisites hold in the process we observe.

By using the peak in derivative thermoanalytical curves, we have three different methods for estimating the activation energy, and all are very simple [5–7]. Agreement among the activation energies estimated by at least two of these three methods should be observed for verification of soundness of the estimation or applicability of the methods, and also verification of the above three prerequisites. Further kinetic analysis to elucidate the mechanism and to estimate the pre-exponential factor can be made by a few methods proposed previously [4–7, 10], and a simple way is to make the derivative master curve by using the following relation.

$$\frac{dC}{d\theta}=\frac{dC}{dt}\frac{dt}{d\theta}=\frac{dC}{dt}\exp\left(\frac{\Delta E}{RT}\right) \tag{10}$$

Relation between dC/dφ calculated by the above equation and φ is the derivative master curve, and the master curves derived by using the results obtained at different heating rates can be superposed on each other. This is also the validation, and because it is similar to isothermal relation between dC/dt and t, the master curve can be analyzed in conventional way. The other simple way is to plot dC/dφ against the reciprocal absolute temperature. The plots can be superposed with each other, because logarithm of φ is proportional the reciprocal absolute temperature [12]. This superposition is also a validation.

The method proposed in this short paper has been applied to thermal shrinkage of polycarbonate films observed at a few different heating rates, and the results are described below.

Experimental

Panlite polycarbonate was supplied in the form of thin film fromTeijin Kasei Co., Ltd.; it contains no additives detectable by IR-spectroscopy. X-ray diffraction measurements of the as-received film samples revealed that the polymer was completely amorphous. The weight averaged molecular weight of the polymer was 4.6×10^4 , estimated from viscosity measurements in tetrahydrofuran solutions. Samples were cold-drawn with a tensile machine at room temperature and under a strain rate of 0.02 min^{-1}. This polycarbonate begins to show necking near 7% strain, and the strain reaches about 80%, when the necking part extends to the whole sample under these drawing conditions. But almost all of strain seems to be recovered by thermal treatment up to above the glass transition temperature.

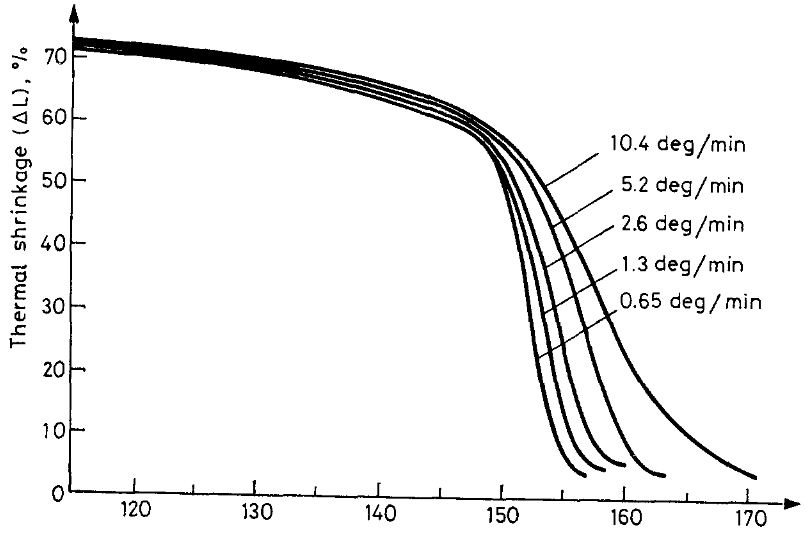

Fig. 1 (*a*) Heating rate-dependence of thermal shrinkage curves

Thermal shrinkage of cold-drawn samples were measured with a thermomechanical analyzer designed and constructed in the laboratory of one of

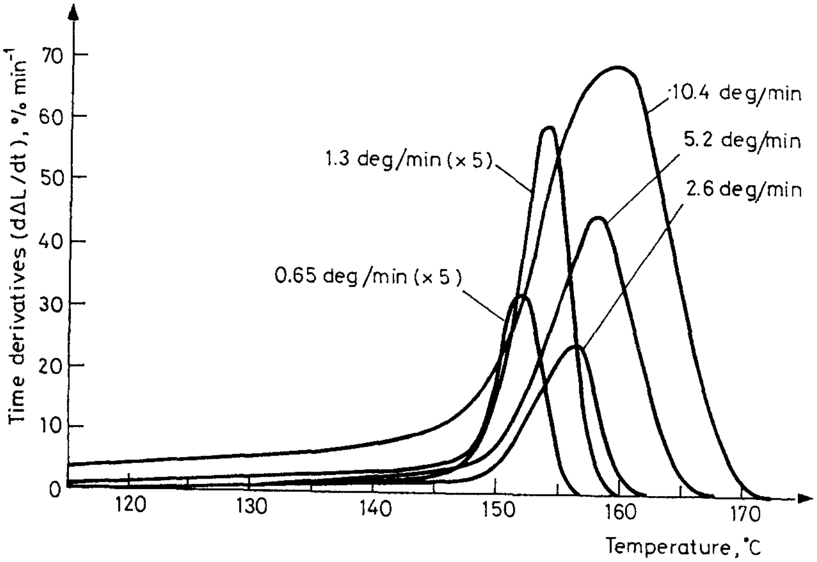

Fig. 1 (*b*) Heating rate-dependence of derivative curves of 80% cold-drawn polycarbonate films

the authors (TK) [13]. The instrument was equipped with a programmed temperature controller so that the sample temperature could be varied linearly with time at several heating rates. The sample dimensions were 10 mm length, 5 mm width and about 100 μm thick. As the samples were very thin, it was not necessary to consider the time lag of sample temperature to the recorded temperature, which was detected with a thin Alumel-Chromel thermocouple situated just beside the sample. A very small external stress of 1×10^5 Pa was usually applied during measurements to keep the sample tight. A signal differentiator for the output of a linear variable differential transformer was also equipped. Thus, the sample temperature, the thermal shrinkage and the rate of shrinkage were recorded simultaneously with a multichannel recorder.

Results and discussion

Figure 1 shows the heating rate-dependence of the thermal shrinkage curves (*a*) and that of the time derivative curves (*b*) around the glass transition of 80% cold-drawn polycarbonate samples. Figure 2 shows the relation of the reciprocal peak temperatures of the derivative curves against the logarithmic heating rate (*a*) and that against the logarithmic peak heights of the derivative curves (*b*). Both plots gave straight lines and the apparent activation energies of the molecular process accompanied with the thermal shrinkage around T_g of this polymer were estimated as 520 kJ/mol from the slope of the straight line (*a*) and as 500 kJ/mol from that of the straight line (*b*). These values correspond well to the reported one of this polymer, 480 ± 20 kJ/mol by Krum and Muller [13] and 430-460 kJ/mol by Matz *et al.*[15, 16].

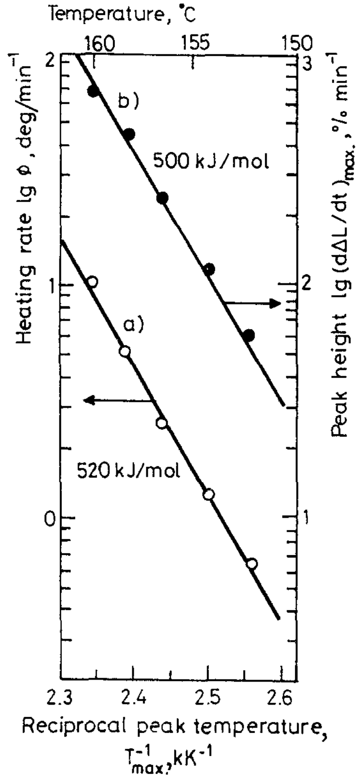

Fig. 2 Plot of the reciprocal maximum temperature of derivative curves against the logarithmic heating rate (*a*) and that against the peak height of the derivative curves of thermal shrinkage of 80% cold-drawn polycarbonate f ilms

It is important to point out here that the two apparent activation energies estimated from the Arrhenius plot and the plot previously proposed by one of the authors (TO) in Fig. 2 were almost the same. This means that the molecular process accompanied with the thermal shrinkage of cold-drawn polycarbonate obeys a kinetics of a rate process as the case reported by Barton on the glass transition of poly(5-ethylresorcinol isophthalate) [17], and the three requisites described in the preceding section are valid.

Before concluding this short communication, we should point out two points. In derivation of the present method, we use the maximum of dC/dt, which is not necessarily the same with the peak in derivative type thermoanalytical curves. For example, the rate of conversion does not reach at its maximum at the peak of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) curves because of thermal lag [17–19], except for DTA and DSC of high thermal response, in which the peak is roughly in coincidence with the maximum rate of conversion. For EGA and evolved gas detection (EGD), the peak of the curves agrees with the maximum rate of conversion, provided that the evacuation is sufficient; otherwise the curve spreads out and becomes diffuse due to accumulation of evolved gas. Therefore the agreement between the peak and the maximum rate of conversion should be taken into accounts in both methods.

Thus, for estimating the activation energy from the maximum rate of conversion, we have, so far, three methods of wide applicability, which do not need any assumption of the reaction mechanism. One is to use the linear relation between the logarithm of heating rate and the reciprocal absolute temperature [5]. The second is based on the linear relation between the logarithm of φ/Tm^2 and the reciprocal absolute temperature. Kissinger first postulated that this relation holds rigorously for the first order reactions and approximately for n-th order reactions [9]. Afterward general applicability of this relation was set forth by the present author [5]. The third relation dealt with in this paper was found to be valid for the first order reaction by Chen and Winer [21]. However this relation hàs general applicability, as proved in this paper.

These three methods are all derived from the fact that the generalized time at the maximum rate of conversion is independent on the heating rate as expressed in the Eq. (8). For deriving this equation an approximation is used as mentioned above, but any other approximation does not need for the third method, while the other two are derived by using approximation furthermore for the integration in the generalized time. The approximation used in the first method is more precise than that in the second method [10], though the second one is the most complicated among the three.

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Zusammenfassung — Die Schätzung der Aktivierungsenergie kann mittels einer neuen Methode erfolgen, bei welcher der Logarithmus der für verschiedene Aufheizgeschwindigkeiten gemessenen maximalen Konversionsgeschwindigkeit als Funktion der reziproken Temperatur aufgetragen wird, da die Konversion bei der maximalen Geschwindigkeit inetwa unabhängig von der Aufheizgeschwindigkeit ist. Das Verfahren wurde beim thermischen Schrumpfen von Polycarbonat angewendet und die geschätzte Aktivierungsenergie liegt in guter Übereinstimmung mit den in herkömmlichen Verfahren ermittelten Werten.