NEW EXPLANATIONS OF IRREGULAR TG DATA ON POLYMERS

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New explanations are given for two types of irregular thermogravimetric (TG) data. A TG relationship between mass and temperature is derived on the basis of migration behavior of bubbles generated in bulk of sample system, and superposed on that derived on the basis of kinetics of the 4th order event, which is superposed on the experimental TG data obtained from three reference papers. This suggests that these TG data are reflecting migration of bubbles. A dependence of TG behavior on heating rate, which is contrary to usual that, is shown and is explained in terms of event-rate determination by boiling.

Introduction

Since its invention, non-isothermal thermogravimetry (TG) has been used widely to study kinetics on thermal decomposition of polymers. But unreasonable or irregular data have been obtained particularly for multiple-stage TG curves. These have not been analyzed, though there are discussions about analyses of a multiple-event consisting of events with different activation energies [1–6]. Recently, we have been tried separation of a multiple-stage TG curve to single-stage TG curves [7, 8]. In the course of the studies, we learned that the initial stage of the triple-stage TG curve of a poly(methylmethacrylate) (PMMA) is superposed on a relationship between mass (M) and temperature (T), derived on the basis of the 4th order event [8]. The shape of some TG curves reflecting water evaporation in literature looks like the 4th order event [9–11]. The thermal decomposition reaction and the evaporation are the 1st and 0th order events, respectively. This discrepancy is interesting. One of the objects of this work is to explain these higher order events. In the present paper, we derive a M-time (t) relation on the basis of migration rate of a gas compound generated in bulk, and show that it can be superposed on that on the basis of the 4th order event.

In most of TG and DSC analyses, isoconversional methods are used [12–15]. When this method is applied to TG data, it is necessary that the species of decomposition products liberating from the reaction system are independent of temperature. This independence is not theoretically kept for TG curves of random decomposition polymers [12]. Recently we obtained non-isoconversional TG data on poly(tetrahydrofuran) (PTHF). Discussion on the analysis of TG data on PTHF is another object of this work.

A bubble migration model

Theory

In the TG measurement, a gas compound evolved in bulk becomes a bubble, migrates to surface, liberates from sample system, and the sample loses the mass. The volume of the bubble, V, depends on the depth, x, as shown in Fig. 1. Therefore we derive the equation of motion by assuming that V is inversely proportional to x:

$$d^2x/dt^2 = -k/x \qquad (1)$$

where k is the constant that includes the coefficient in V proportional to $1/x$, the inverse of mass of bubble, and the density of medium. Algebraic solution of differential Eq. (1) is very complicated and is unsuitable for TG data analysis. Therefore, we tried to obtain the plots of x *vs.* t by numerical solution. Figure 2 shows the plots for the bubble migration model and the 4th order event model by use of software [16]. The plots for the 4th order event model is its mirror image *vs.* $kt=0.6$. Therefore, the ordinate denotes the conversion, C, but the abscissa does not denote the real kt value and does ($0.6-kt$) value. When the concentration of bubble compound is uniform, C is proportional to x. Accordingly the good superposition of two equations suggests that the bubble migration appears as the 4th order event in TG curves. Equation (1) multiplied by $2(dx/dt)$ becomes:

$$dx/dt = (2k)^{1/2}f(x) \qquad (2)$$

where $f(x)=[\ln(L/x)]^{1/2}$ and L is the depth of the sample system. Equation (2) is applicable to an isoconversional method with $(2k)^{1/2}=A\exp(-E_a/RT)$ where A, E_a and R are the frequency factor, the activation energy, and the gas constant, respectively. The migration from bulk to surface is thermal motion and therefore k is an Arr-

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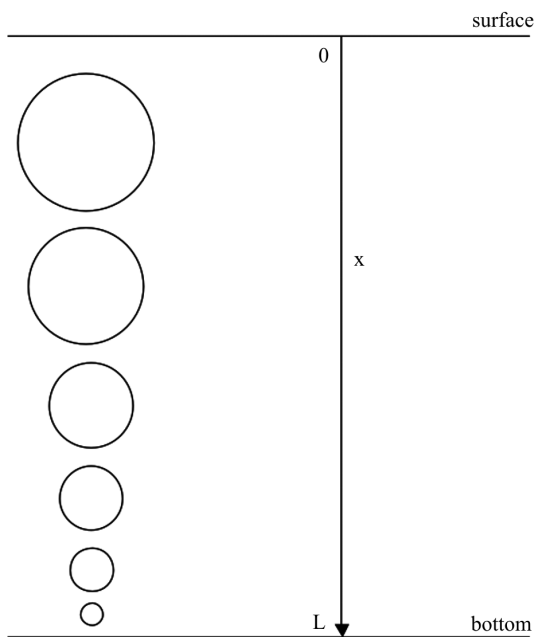[*]   Author for correspondence: c-taka@nda.ac.jp
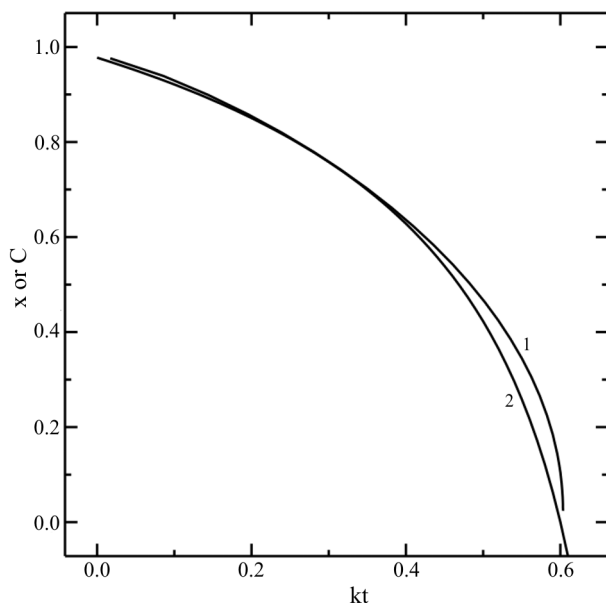
Fig. 1 Migration of bubble from bottom to surface

Fig. 3 TG plots obtained from $\square$ – [9], $\circ$ – [10] and $\triangle$ – [11];
— – TG curves drawn by Eq. (13)

$$M/M_0 = 1/[1+\exp(p-q/T)]^{1/3} \quad (3)$$

$$p = \ln(3AE_a/aR) - 5.331, \; q = 1.052E_a/R$$

where a is the heating rate. The E_a and A values were evaluated by fitting Eq. (3). The agreement between the experimental plots and the curves based on Eq. (3) suggests the bubble migration model is available to TG data in [9–11]. The values of activation energy are between 118 to 120 kJ mol^{-1} and are close to that of PMMA, equal to 122 kJ mol^{-1} [8] that is the E_a value in evolution of MMA before the main depolymerization.

Non-isoconversional TG data

Figure 4 shows TG curves of PTHF (Teratan2900) recorded with the heating rates of 5 K min^{-1} (1) and 10 K min^{-1} (2) by use of a Perkin Elmer TG-7 instrument (sample size, about 1 mg; flow gas, N$_2$). The dependence of TG behavior on heating rate in Fig. 4, that is, it is contrary to the usual heating rate dependence that the faster the heating rate, the larger the mass loss at a given temperature. The thermal decomposition of PTHF is the typical Simha-type random decomposition [12]. Simha equation is given by:

$$\mathrm{d}C/\mathrm{d}(kt) = (D-1)(1-C) - [(N-D)(D-1)/N]\exp(-Dkt) \quad (3)$$

where k is the rate constant and $(D-1)$ is the degree of polymerization of the largest evaporated compound. And N is the degree of polymerization of the starting polymer. When N is much larger than D and t is relatively longer, Eq. (3) is approximated to the following equation: $\mathrm{d}C/\mathrm{d}(kt) = (D-1)(1-C)$, that is,

Fig. 2 Plots for the 4th order model:
$1 - C = 2.05\{1 - [10(0.6-kt)+1]^{-1/3}\}$ and the bubble migration model: $2 - -\mathrm{d}^2x/\mathrm{d}(10kt)^2 = 0.05/x$

henius-type constant. A half of the real activation energy is obtained by isoconversional method. It suggests that the TG curve is a slow-down curve.

Application to experimental TG data

Figure 3 shows the hand-made TG plots using TG curves in [9–11], and the TG curves based on the 4th order event, which are drawn by the following equation using the Doyle approximation [12] for p-function:
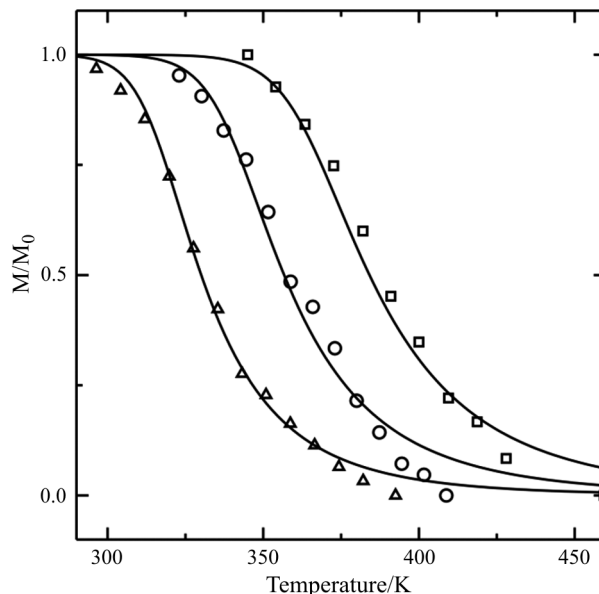
Table 1 Estimation of E_a and A by fitting Eq. (3)

Sample	a/K min^{-1}	p	$q \cdot 10^{-2}$	E_a/kJ mol^{-1}	$A \cdot 10^{-15}$/min^{-1}	Ref.
PVal	1	44	150	118	44.7	9
TMOS	10	48	152	120	240	10
lyocell	10	41	150	118	2.22	11

$-dM/dt = k(D-1)M$. The rapid evaporation occurs at boiling temperature. Therefore, mass loss mentioned above is proportional to difference in temperature, that is, the heating rate, a, for a constant time:

$$\ln(M_0/M) \propto (D-1)ka \qquad (4)$$

Table 1 shows the k and D values derived by use of Eq. (4), assuming that the proportional constant is unity and referring the experimental data in Fig. 4. The calculated E_a value equal to 76.4 kJ mol^{-1} is close to the E_a value obtained from an isothermal TG technique in [12, 17].
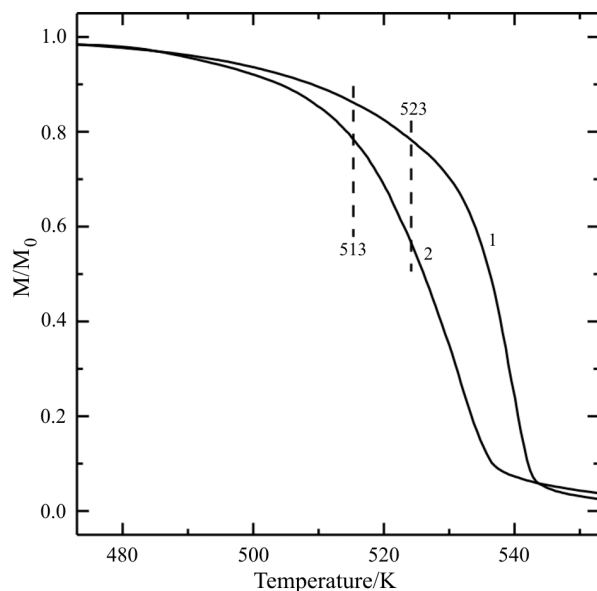
bubble is inversely proportional to the depth, a differential equation was derived. The numerically solved plots of M/M_0 *vs.* T are superposed on the plots based on 4th order event. These are superposed on different three experimental TG data in literature. These experimental TG data might be reflecting bubble migration rate. The TG behavior of randomly decomposed polymers is not isoconversional. Assuming the evolution rate is determined by boiling, TG data of PTHF were analyzed. The obtained TG parameters are agreed with those obtained from isothermal TG experiments. It means non-isoconversional TG behaviors can be explained in terms of the TG behavior attributed to boiling.

Fig. 4 TG curves of PTHF, recorded at the heating rates of 1 – 5 K min^{-1} and 2 – 10 K min^{-1}

Conclusions

The new explanations were proposed for two types of irregular TG data. One is based on migration rate of a bubble generated in bulk. Another is based on evolution rate determined by boiling. Assuming the volume of

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