Comparative Study of Various Methods for Thermogravimetric Analysis of Polystyrene Degradation

H. NISHIZAKI, *Government Industrial Development Laboratory, Hokkaido, Sapporo 060-01, Japan,* K. YOSHIDA, *Engineering Research Institute, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan,* and J. H. WANG, *Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan, Republic of China*

Synopsis

Various methods of thermogravimetric analysis were compared in case of polystyrene degradation. The reaction order, the activation energy and the preexponential factor were evaluated from common TG curves experimentally obtained. In most cases a 5-mg sample of polystyrene with 110,000 molecular weight was decomposed at heating rate of 10°C/min. The reaction was found under this experimental condition to be of first order with activation energy of 61.0 kcal/mole, though there were slight differences depending on the analytical methods used.

INTRODUCTION

The thermogravimetric analysis (TGA) is widely used as a method to investigate the thermal decomposition of polymers and to determine the kinetic parameters such as activation energy, preexponential factor, and reaction order.

Detailed descriptions of method are not given here, since there is an abundance of literature on the subject. In particular, two reviews written by Flynn and Wall[1] and Reich and Levi[2] covered excellently all important techniques so far available for evaluating the kinetic parameters from the TGA traces.

The TGA methods are classified into two groups; integral and differential methods. It is, however, not clarified yet which method is the most suitable for describing the thermal decomposition of polymer. In this study, therefore, the thermal decomposition of polystyrene was made to test various kinds of TGA methods.

METHODS FOR DETERMINATION OF KINETIC PARAMETERS

The isothermal rate of conversion dC/dt in the process of thermal decomposition is generally expressed by

$$\frac{dC}{dt} = kf(C) \tag{1}$$

The conversion C is defined by

$$C = 1 - W/W_0 \tag{2}$$

where W_0 and W represent initial weight and weight at any time, respectively.

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The reaction rate constant k is expressed by the following Arrhenius equation.

$$k = A \exp(-E/RT) \tag{3}$$

where E represents activation energy and A represents preexponential factor.

On the other hand, $f(C)$ is some temperature-independent function of conversion and is expressed in analogy to simple cases in homogeneous kinetics as

$$f(C) = (1 - C)^n \tag{4}$$

where n is the apparent order of reaction.

Substitution of eqs. (3) and (4) into eq. (1) gives

$$\frac{dC}{dt} = A \exp\left(\frac{-E}{RT}\right)(1 - C)^n \tag{5}$$

In the TGA the rate of heating $\beta = dT/dt$ is kept to be constant. Thus,

$$\frac{dC}{dt}\beta = A \exp\left(\frac{-E}{RT}\right)dT \tag{6}$$

Modification of eq. (6) becomes

$$\frac{dC}{(1 - C)^n} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)dT \tag{7}$$

Introducing the initial condition given by

$$C = 0 \qquad \text{at} \qquad T = T_0$$

eq. (7) becomes

$$F(C) = \int_0^C \frac{dC}{(1 - C)^n} = \frac{A}{\beta}\int_{T_0}^T \exp\left(\frac{-E}{RT}\right)dT = \Phi \tag{8}$$

where $F(C)$ is integrated function of conversion and Φ is temperature integral.

Integral Methods

The TG trace gives the relationship between C and T. In the integral methods this relation is used to integrate the eq. (8) for determining the proper values of A, E, and n. In this connection, there have been several methods which make differences in the approximate integration of the exponential integral. Representative methods are summarized in Table I, where the methods using the maximum rate of conversion[5] and that using two TG curves[7] are included.

Differential Methods

In principle, in integral methods, $F(C)$ is first determined by assuming the value of n, and from its change with temperature E and A are calculated so as to satisfy the eq. (8). On the other hand, the differential methods are to determine the values of A, E, and n satisfying eq. (6) by use of the relationship between dC/dT and T, which is given by the differentiation of TG curves.

TABLE I
Representative Integral Methods

Authors	Equations	
van Krevelen et al.[3]	$\ln\left(\frac{(1-C)^{1-n}}{1-n}\right) = \ln\left[\frac{\mathrm{AR}}{\beta\mathrm{E}}\left(\frac{0.368}{T_m}\right)^{E/RT} m(T_m+1)\right.$ $(n \neq 1)$ $\ln\lvert\ln(1-C)\rvert + \frac{E}{R(T_m+1)}\ln T$ $(n = 1)$ where T_m is the temperature at maximum conversion rate dC/dt.	(9)
Coats and Redfern[4]	$\log\frac{\mathrm{C}}{T^2} = \log\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right) - \frac{E}{2.3R} \times \frac{1}{T} \quad (n \cong 0)$	(10)
Horowitz and Metzger[5]	$\ln\ln(1-C) \cong \ln\frac{AE}{\beta R} - 5.33 - \frac{1.052}{T_s} + \frac{1.052E\theta}{RT_s2} \quad (n \neq 1)$ where T_s is the temperature at maximum conversion rate; $\theta = T - T_s$; and $C_s = (n)^{1/(1-n)}$ is the conversion rate at T_s.	(11)
	$\ln\ln(1-C) \cong \frac{E\theta}{RT_s2} \quad (n = 1)$ where T_s is the temperature at $1 - C = 1/e = 0.368$; and $\theta = T - T_s$.	(12)
Reich and Levi[6]	$\left.\begin{matrix} \ln[\ln(1-C)] & (n = 1) \\ \ln C \quad (n = 0) & \end{matrix}\right\} \cong -\frac{E}{RT} + \ln\left(\frac{A\Delta T}{\beta}\right)$ where ΔT is the temperature intervals for reading of C.	(13)
Reich[7]	$E = \frac{4.6\log(\beta_2/\beta_1)(T_1/T_2)^2}{(1/T_1 - 1/T_2)}$	(14)
Ozawa[8]	$-\log\beta_1 - 0.457\frac{E}{RT_1} = -\log\beta_2 - 0.457\frac{E}{RT_2} = \cdots$ $\left\{\begin{matrix} \log[(1-C)^{1-n} - 1] = \log\beta & (n \neq 1) \\ \log\lvert n(1-C)\rvert = \log\beta & (n = 1) \end{matrix}\right.$	(15)

There have been also several methods which are different in the approximation. Representative methods are listed in Table II, where the method using several weights of samples[1] and that using the difference of differentiated values of a TG curve[12] are also referred.

EXPERIMENTAL

The reactive substance used in this study was a white powder of standard polystyrene with the molecular weight of 110,000, which is produced by Pressure Chemical Co. Ltd. The sample to be studied was placed in a platinum sample cell of 5 mm $\phi \times 3$ mm h and the white alumina powder of the same weight was

TABLE II
Representative Differential Methods

Authors	Equations	
Kissinger[9]	$n(1-C)_m^{n-1} \cong 1 + (n-1)\dfrac{2RT_m}{E} \quad (n \neq 1)$ $\ln(1-C)_m = \left(1 - \dfrac{2RT_m}{E}\right) \quad (n = 1)$	(16)
	where $(1-C)_m$ is the value at temperature T_m that provides the maximum conversion rate, $n = 1.26S^{1/2}$; and S is the shape index $\doteq (d^2C/dt^2)_1/(d^2C/dt^2)_2$.	(17)
Friedman[10]	$\ln\beta\, dC/dt = \ln Af(C) - E/RT$ $f(C) = (1-C)^n$	(18)
Chatterjee[11]	$\log\left(\dfrac{-dW}{dt}\right)_1 - \log\left(\dfrac{-dW}{dt}\right)_2 = n(\log W_1 - \log W_2)$	(19)
	where W_1 and W_2 are the residual weight at the same temperature of two kinds of initial sample weight, respectively.	
Freeman and Carroll[12]	$\dfrac{\Delta\log\beta\, dC/dT}{\Delta\log(1-C)} = n - \dfrac{E}{2.3R}\dfrac{\Delta(1/T)}{\Delta\log(1-C)}$	(20)
	where Δ is the difference value for constant $\Delta(1/T)$.	

placed in a reference cell. Then, both cells were immersed in a heat bath, and the reaction was initiated by supplying heat to the bath in a prescribed rate of heating. The heating was continued up to the moment when the sample ceased decreasing in the weight.

The heating rate at 5, 10, 20, and 40°C/min and the sample weight with 3, 5, and 8 mg were tested. The continuous record was taken of the change in both the temperature and the weight of sample cell and of the differential change in the weight.

EXPERIMENTAL RESULTS AND DISCUSSION

A representative result is shown in Figure 1, where the TG curves for the thermal decomposition of a 5-mg polystyrene sample are shown with several heating rates.

Various methods summarized in Tables I and II were applied one by one to the experimental results. Figure 2 shows the relationship given by eq. (9) of van Krevelen et al.[3] Assuming the reaction order to be 1, a linear relation was obtained, and the activation energy was calculated from the slope. Figure 3 shows the relationship proposed by Coats and Redfern.[4] In this method all reactions are assumed to behave as zero order at low conversion. Horowitz and Metzger[5] presented eqs. (11) and (12) to obtain both the reaction order and the activation energy from experimental data. The relation is shown in Figure 4. There is a method proposed by Reich and Levi,[6] where the TG curves for two different heating rates are needed. Figure 5 shows the results of application of eq. (13). In case the reaction order should be assumed to be 1, the data were found to be

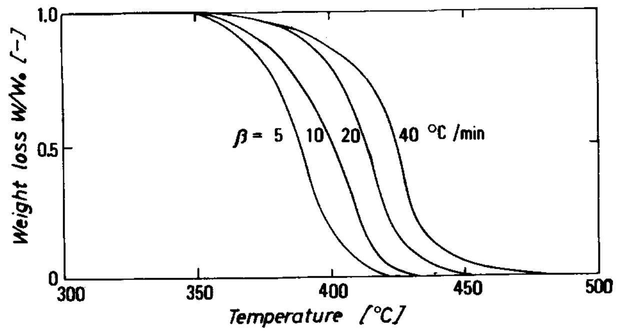

Fig. 1. TG curves for various heating rates. M_n = 110,000; W_0 = 5 mg.

better arranged than in the case for $n = 0$. The relationship between conversion and temperature is shown for the case of $n = 1$ in Figure 6, and the activation energy is obtained from the slope. Reich[7] also pointed out that eq. (14) may be used to calculate simply the activation energy. The method developed by Ozawa[8] permits the determination of activation energy through the TG curves

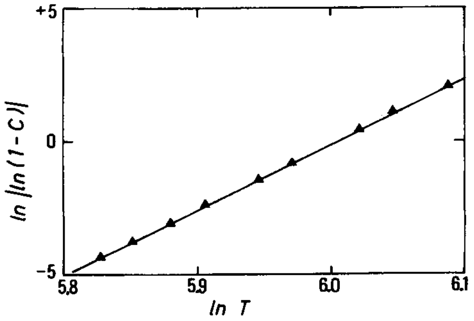

Fig. 2. Application of van Krevelen's method to experimental data. T_m = 407°C for n = 1.0.

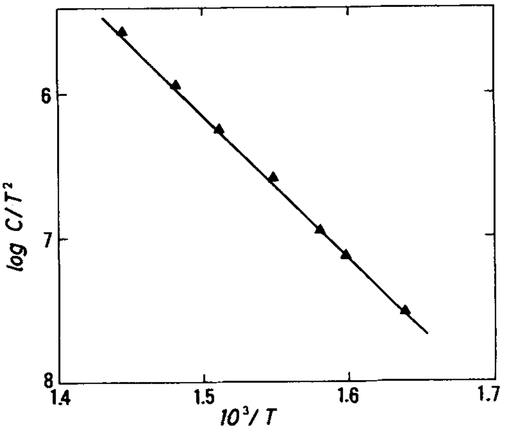

Fig. 3. Relationship obtained by Coats and Redfern's method. β = 10°C/min, n = 0 assumed.

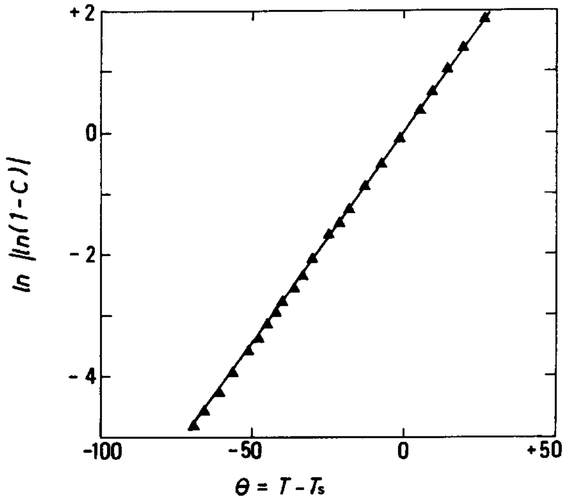

Fig. 4. Application of Horowitz's method to experimental data. $\beta = 10°C/min$, $(n)_{calc} = 1.0$.

to be obtained by changing the heating rate. The relations are shown in Figure 7. In order to obtain the order of reaction, plotting of data was made as shown in Figure 8, which shows so good linear relations as to conclude n to be 1.

Kissinger[9] presented eqs. (16) and (17) to calculate kinetic parameters from the differentiated values of conversion. Figure 9 shows the relations given by eq. (18) of Friedman's method.[10] The horizontal relation shown by Figure 9(b) results in determining the order n to be zero and the intercept gives the activation energy. Provided with TG curves for two runs differing in their initial weights, the order n may be determined from eq. (19) presented by Chatterjee.[11] The difference-differential method of Freeman and Carroll[12] is the most widely used method for the kinetic analysis of TG data. Figure 10 shows the plotting for determination of both the activation energy and the reaction order.

The results mentioned so far are summarized in Table III. The order of reaction is found to be 1 for all of the different methods employed, except that of Friedman. This may be due to the fact that the Friedman's method required two-step figure drawing resulting in considerable errors. As for the activation energy, the value obtained by the method of van Krevelen et al. is extremely low.

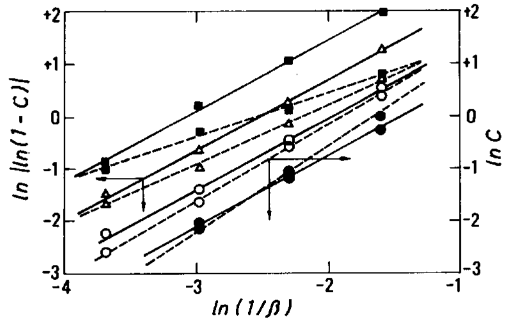

Fig. 5. $\ln|\ln(1 - C)|$ or $\ln C$ vs. $\ln(1/\beta)$ for Reich's method. (●) 390°C, (○) 400°C, (△) 410°C, (■) 420°C; (–) $n = 1$, (- - -) $n = 0$.

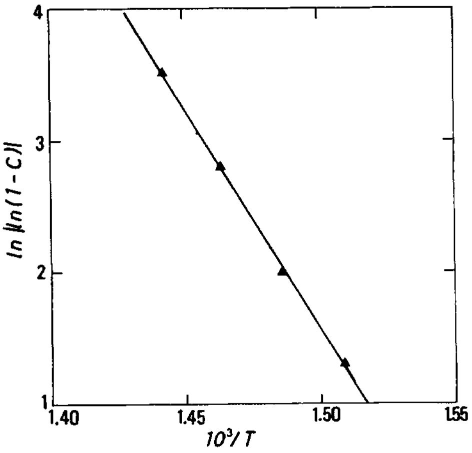

Fig. 6. Estimation of E by Reich's method; $n = 1.0$.

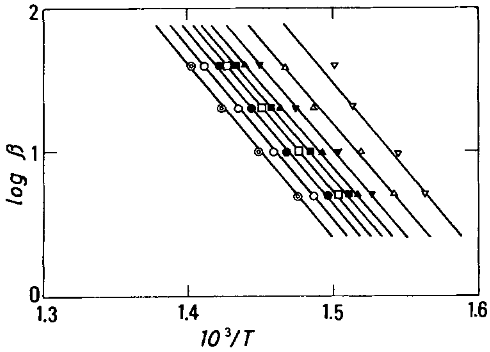

Fig. 7. Logβ vs. reciprocal absolute temperature for Ozawa's method. $(1 - C)$: (▽) 0.9, (△) 0.8, (▼) 0.7, (▲) 0.6, (■) 0.5, (□) 0.4, (●) 0.3, (○) 0.2, (◎) 0.1.

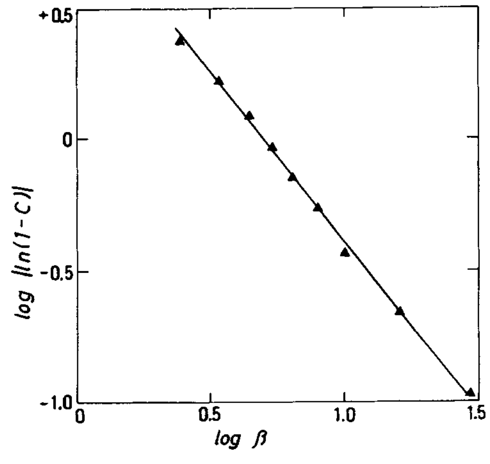

Fig. 8. Relationship obtained by Ozawa's method for $n = 1.0$.

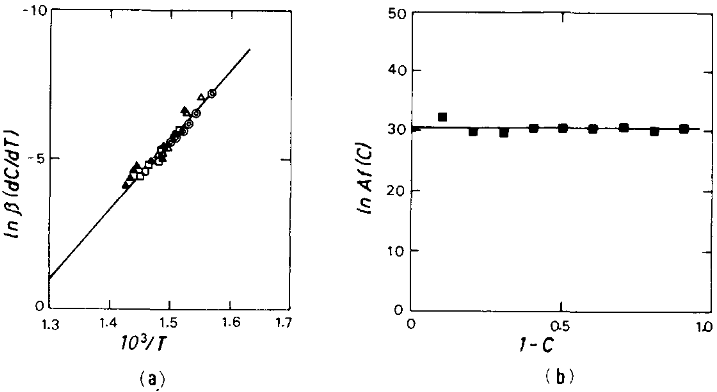

Fig. 9. Relationship obtained by Friedman's method (a) for estimation of E: β (°C/min) (◎) 5, (△) 10, (□) 20, (▲) 40; (b) for estimation of n and A for n = 1.0.

Excluding this extraordinarily low value, therefore, the activation energy with the reaction order being determined to be 1 was found lying in the range of 61.0 ± 11.0 kcal/mole. Thermal decomposition of polystyrene has been studied by Anderson and Freeman,[13] Kokta et al.,[14] Murata and Makino,[15] and Kuroki et al.[16] Anderson and Freeman reported that the reaction behaves as zero order in the initial stage of degradation, while the reaction is subject to change to first order with increase of conversion. Kokta et al. similarly showed that there are two stages of degradation, one predominant over the first part of reaction with zero order, and the other at the rest with first order. Including other two studies the activation energy is, respectively, 60.0 ± 5.0, 50.0 ± 5.0, 60.0, and 54.7 kcal/mole in case that the reaction order is considered to be unity, and these values fall within the limit above mentioned.

On the other hand, both results of activation energy reported by Anderson and Freeman and Kokta et al. for the initial stage of reaction, where the reaction order is zero, are 46.0 and 33.0 ± 5 kcal/mole. In the method developed by Coats and Redfern the order is assumed to be zero in the stage of low conversion. Application of experimental data to this method gives the activation energy of 46.0 kcal/mole. It is interesting to note that this value together with that of 35.0 kcal/mole reported by Coats and Redfern themselves agrees fairly well with those so far available at the low-conversion stage.

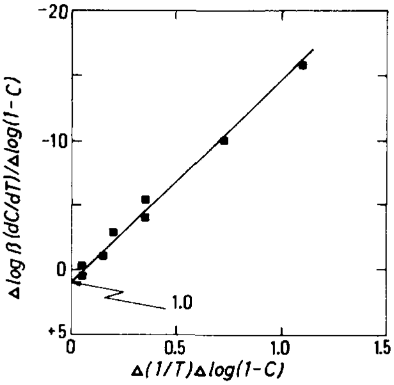

Fig. 10. Application of Freeman and Carroll's method to experimental data. β = 10°C/min.

TABLE III
Comparison of Kinetic Parameters Obtained by Various Methods
(common experimental conditions: $W_0 = 5$ mg, $\beta = 10$°C/min)

Methods	Reaction order n	Activation energy E, kcal/mole	Preexponential factor A, min^{-1}	Remarks
I. Integral method				
van Krevelen et al.[3]	1.0[a]	20.4	—	
Coats and Redfern[4]	0 (assumed)	46.0	6.3×10^{14}	
Horowitz and Metzger[5]	1.0[b]	65.9	8.5×10^{20}	
Reich and Levi[6]	1.0[b]	67.2	3.7×10^{22}	
Reich[7]	—	50.0	—	$\beta = 5, 10$°C/min
Ozawa[8]	1.0[a]	50.5	8.1×10^{15}	$\beta = 5, 10, 20, 40$°C/min
II. Differential method				
Kissinger[9]	1.0[b]	67.8	—	
Friedman[10]	0[a]	48.3	1.8×10^{13}	$\beta = 5, 10, 20, 40$°C/min
Chatterjee[11]	0.8[b]	59.4	1.1×10^{17}	$W_0 = 3, 5, 8$ mg
Freeman and Carroll[12]	1.0[a]	69.0	1.8×10^{20}	

[a] Estimated via data plotting.
[b] Calculated by equations.

As shown by Kokta et al.[14] it is known that the kinetic parameters are possibly affected by experimental conditions such as molecular weight, sample weight, and heating rate. In this article we treated mostly a representative experimental condition to find out the effect of analytical methods only. Further study must be made in various systems to find out the clear effect and to identify its substantial reason.

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