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Analysis of thermal decomposition behaviors with consecutive reactions by TG

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Abstract

Thermal decomposition behaviors of a fluororubber are observed with linear heating mode at constant rate, controlled rate mode and isothermal mode of TG/DTA, and, with isothermal mode of TG/mass-spectrometer. The results suggest that this material decomposes with, at least, three consecutive reactions. From the results of TG/DTA and TGMS in isothermal mode, it is considered that the first reaction is the first-order reaction, the second reaction is chain reaction and the last reaction is vaporization of residue. Supposing these three consecutive reactions, the decomposition behaviors of the rubber is simulated. The observed curves of fraction of mass loss, α, against time, t, are well reproduced by the simulation. The relationship between $d\alpha/dt$ and α is reproduced also, though the differences between observed and the calculated values of $d\alpha/dt$ are slightly larger than noise level of $d\alpha/dt$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Isothermal thermogravimetry with mass-spectrometry; Method of kinetic analysis; Kinetics of thermal decomposition reactions; Kinetic analysis of consecutive reactions; Fluororubber

1. Introduction

Thermogravimetry (TG) is a useful tool for kinetic analysis of thermal decomposition reactions. If a material decomposes with a simple reaction and when the mass loss is observed with conventional linear heating TG at constant rate (LHTG), a single step mass loss will be observed. In such cases, kinetic analysis can be done using the relations between mass loss, rate of mass loss and temperature obtained with several heating rates [1–5].

However, a single step mass loss obtained in LHTG does not necessarily mean that the decomposition reaction is a single elementary process. If a material decomposes with several consecutive reactions and the differences of activation energies are small, mass loss observed in LHTG will become a single step change. If a method of kinetic analysis for a single elementary process is applied to the data of LHTG mode of such material, the obtained activation energy will change with fraction of mass loss. If the conditions of measurements are not adequate, the activation energy will change with fraction of mass loss also. Controlled rate TG (CRTG) is a useful tool to distinguish these two cases. However, if a material decomposes with consecutive reactions, it is difficult to analyze the results of CRTG kinetically because the

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rate of mass loss for each reaction is not constant. In order to analyze consecutive reactions kinetically, isothermal TG measurements (iso-TG) are the most useful method.

The rate equations are written with mole fractions, in general. On the other hand, only the relations between the total mass loss, the rate of total mass loss and time are obtained in iso-TG. Therefore, it is necessary to relate the mole fractions to the fractions of mass loss and the fractions of residual mass. To discuss the relation between total mass loss and each reaction, simulation becomes necessary. The plot of the rate of mass loss against fraction of mass loss is useful to construct the simulation model of the consecutive reactions. The data of TG with mass-spectrometer (TGMS) is a powerful tool too.

It is found that a fluororubber decomposes with several consecutive reactions. The thermal decomposition behaviors of this rubber were observed with TG and TGMS. Using the results obtained in iso-TG, simulation for quantitative analysis was tried. Experimental results and a method for kinetic analysis are shown in this paper.

2. Experimental

The sample used is a crosslinked rubber. Its chemical structure before crosslinking is shown below.

$$R{-}({-}CF(CF_3){-}CF_2{-}O{-}CF(CF_3){-}CF_2{-})_n{-}R$$

where R is $CH_2{=}CH{-}SiH_2{-}$. As this material is insoluble, there is no further information.

Thermal decomposition behaviors of this material in nitrogen are observed. The modes of measurements used are LHTG, CRTG and iso-TG. The thermobalance used in this study is a TG-differential thermal analysis (DTA) simultaneous apparatus (Thermo Plus 8120, Rigaku Co., Ltd.). Mass spectra of vaporized materials are observed using Thermo Plus 2/8120D with mass spectrometer, HP6890-5973A.

Heating rate used in LHTG were 0.5, 1, 2, 5 and 10 K min^{-1}. If the mass of sample is too much, the heating rate of the sample cannot be kept constant because of the temperature change by heat of decomposition reaction [6]. From this reason, the initial sample mass used were 1.4 mg for 0.5 and 1 K min^{-1}, and 0.8 mg for 2, 5 and 10 K min^{-1}. Under these conditions, heating rates of the samples were kept constant.

In CRTG mode, the sample was heated with 20 K min^{-1} at first, and then the rate of mass loss was kept at 0.136% min^{-1}. This was the maximum rate to keep the rate of mass loss constant. The initial sample mass was 5.35 mg.

For iso-TG, the sample was initially heated with 20 K min^{-1} and then the temperature was kept constant. The mean temperatures of isothermal measurements were 390.2, 400.7 411.7 and 420.8°C, and the initial sample mass were between 2.7 and 3.0 mg. Mass spectra were obtained with isothermal mode of TGMS (iso-TGMS) at 420°C after heating with 20°C min^{-1}. The initial sample mass was 16.89 mg and the carrier gas was helium. Mass spectra were measured every second.

3. Results

The fraction of mass loss, α, is defined as $\alpha=(w_i-w(t))/(w_i-w_f)$, where w_i is the initial sample mass, $w(t)$ is the mass of the sample at time t, and w_f is the final residual mass. The fraction of residual mass, X, is equal to $1-\alpha$. The curve of α against temperature, T, obtained in LHTG showed a single-step mass loss and the residual mass was near zero. If the decomposition proceeds a single elementary process, the plots of α or X against inverse of T can be superposed if they are shifted along the $1/T$ axis [4–6]. Fig. 1 shows the result of superposition on the curve obtained with 2 K min^{-1}. Though all curves are smooth and show a single-step mass loss, the entire curves cannot be superposed. Except the region where α is from 0.3 to 0.4, the curves obtained with lower heating rates are shifted to the low temperature side. This means that, if a simple reaction is assumed, the obtained activation energy, E, will show a maximum at $\alpha\approx0.35$. Fig. 2 shows the relation between α and T obtained in CRTG with 0.136% min^{-1} of the rate of mass loss. This result cannot be explained by a simple reaction.

If the decomposition proceeds with a single elementary process, it is possible to superpose the curves of α against logarithm of t obtained in iso-TG by the shift along ln t axis. Fig. 3 shows the result of superposition. In this figure, the curves obtained at 390.2, 411.7 and 420.8°C are superposed on the curve

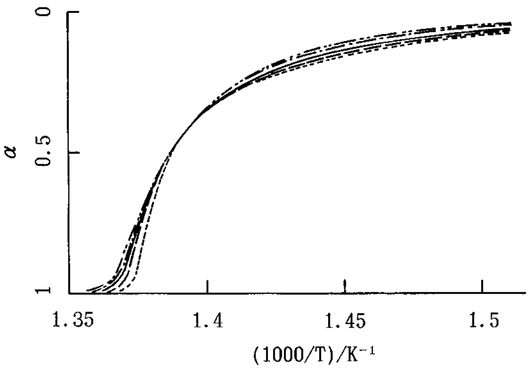

Fig. 1. Plots of α against 1000/*T* obtained in LHTG. Curves are superposed to 2 K min^{-1} (solid line) from 0.5 K min^{-1} (dotted line), 1 K min^{-1} (broken line), 5 K min^{-1} (dotted broken line) and 10 K min^{-1} (double dotted broken line).

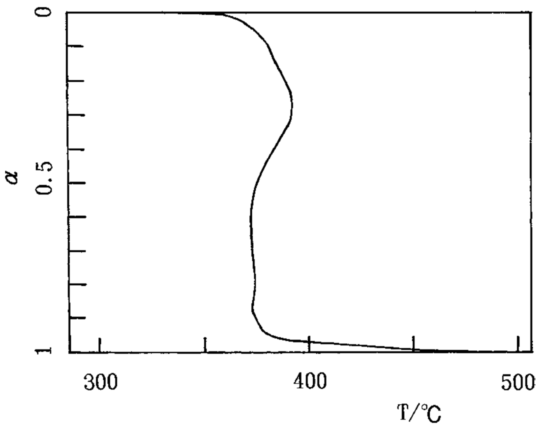

Fig. 2. The relationship between *T* and α obtained in CRTG. dα/d*t* was 0.136% min^{-1}.

obtained at 400.7°C. As the entire curves cannot be superposed, the part of curves where α is above 0.5 is superposed. The value of *E* of this superposition is 206 kJ mol^{-1}. This value will be the mean value in the region where α is above 0.5.

To analyze the data of iso-TG, the plot of dα/d*t* against α is useful. If the decomposition proceeds with a single elementary process, the curves of dα/d*t* against α can also be superposed. Fig. 4 shows the result of superposition to 400.7°C. 206 kJ mol^{-1} is used for this superposition. dα/d*t* has a minimum, a maximum and a shoulder. Figs. 2 and 4 suggest that this rubber decomposes with, at least, three reactions.

In the region where α is below 0.2, dα/d*t* decreases linearly with increasing α. Linear relationship between dα/d*t* and α suggests that the first reaction is the first-order reaction. If dα/d*t* is linearly extrapolated to zero, the mean value of α at the point where dα/d*t* becomes zero is 0.30. However, as the noise level of dα/d*t* is about ±0.02 to 0.03% min^{-1}, there is a possibility that the reaction is of the second order. If the first reaction is the first- or the second-order reaction, it will cause the rise of temperature in CRTG curve. The reaction which shows the maximum in the relation between dα/d*t* and α, is chain reaction (autocatalytic reaction) or random scission of main chain of polymers. These reactions lower the temperature of sample in CRTG

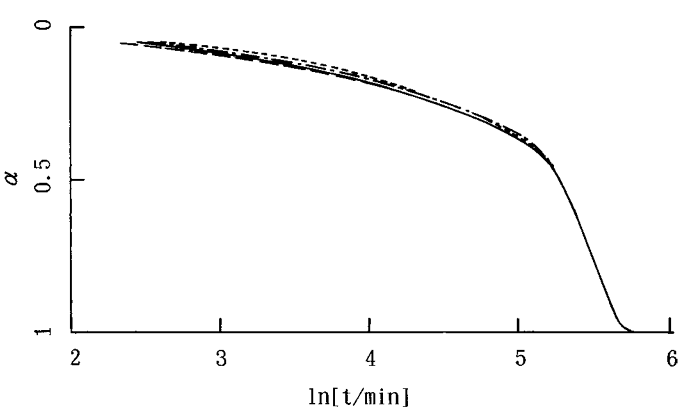

Fig. 3. Plots of α against logarithm of *t* obtained in iso-TG. Curves are superposed to 400.7°C (solid line) from 391.2°C (broken line), 411.7°C (dotted broken line) and 420.8°C (dotted line).

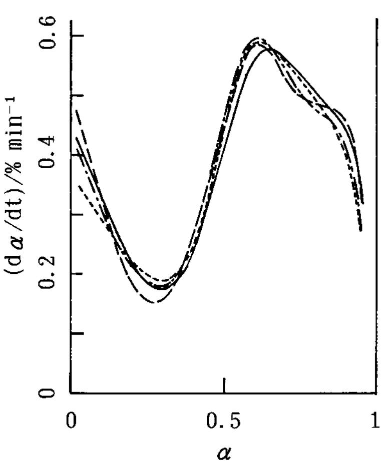

Fig. 4. Plots of dα/dt against α obtained in iso-TG. Curves are superposed to 400.7°C (solid line) from 391.2°C (broken line), 411.7°C (dotted broken line) and 420.8°C (dotted line).

mode. dα/dt shows a shoulder where α is about 0.8. The origin of the shoulder will be discussed later.

Many fragments are observed in the mass spectra obtained in iso-TGMS. For the analysis of decomposition reaction, the plot of intensity of each fragment against α is useful. This plot shows the relation between the rate of production of each fragment and α. The curve of intensity of each fragment against α is classified into four fundamental types and three complex types. Fig. 5 shows four fundamental types.

The intensity of type A decreases with increasing α. This behavior corresponds to the decrease of dα/dt observed in iso-TG. The relation between the intensity of type A and α is almost linear and it does not trail long. This suggests again that the first reaction is the first-order reaction. The m/z of the fragment of type A are 59, 77, 91, 96 and 163. From these values and the chemical structure of the original polymer, the structures of the fragments of type A are considered to be $C_aSi_bH_cF_d$ where a and c are equal to or larger than 1. This means that the crosslinked structure of vinylsilane decomposes by the first reaction.

The intensity of type B and B′ shows a maximum and a shoulder. The intensity of the shoulder of type B is about 0.7 times of peak and the intensity of the shoulder of type B′ is almost equal to that of peak. The value of α at maximum intensity is about 0.6 and that at shoulder is about 0.8. These points correspond to the maximum and the shoulder of dα/dt observed in iso-TG. The reaction, which shows a peak in the plot of intensity of fragment against α, is chain reaction or random scission of main chain. The m/z of the fragment of type B are 31, 44, 85, 100, 131 and 150. The m/z of type B′ is 69. The structures of fragments of type B and B′ are supposed to be mainly $C_kF_lO_m$ and SiF_n.

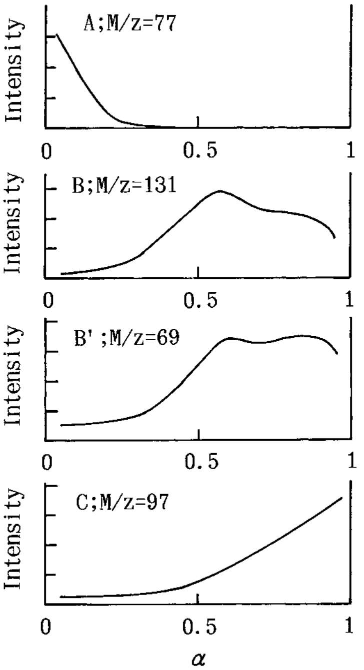

Fig. 5. Four fundamental types of the curves of the intensity of fragments obtained in iso-TGMS against α.

The intensity of the fragment of type C increases with increasing α. It is considered that the concentration and/or quantity of the material, which causes this behavior, increases when the reaction proceeds, and, at the same time, it vaporizes. The ‘reaction’ which shows such behavior is considered to be the vaporization of residue. This will be the last ‘reaction’. If the last reaction is vaporization, it becomes zeroth-order ‘reaction’. The m/z of the fragments of type C are 97 and 147. The structures of the fragments of type C are supposed to be mainly $C_kF_lO_m$. Namely, the structures of the vaporized materials of the second and the last reaction are similar. Besides these four types, there are three complex types, which are A+B, A+B′ and A+C. The m/z of the fragments of type A+B, A+B′ and A+C are 81, 47 and 119, respectively.

About shoulder after peak, there are two possibilities. One possibility is the overlap of the second reaction with the last, zeroth-order reaction like vaporization. Another possibility is the presence of the third reaction before the last reaction. If there is the third reaction, it will be chain reaction or random scission of main chain. The temperature in CRTG mode becomes almost constant in the region where α is above 0.6. If the temperature ascent by the later half of the second reaction in CRTG mode is canceled by the temperature descent by former half of the third reaction, the temperature in CRTG will become almost constant. There is another possibility. If the first and the second reactions in CRTG mode proceed faster than iso-TG mode because of temperature ascent, and if the last reaction is zeroth-order, the temperature in CRTG mode will also become almost constant. In the following treatment, supposing that this fluororubber decomposes with three consecutive reactions, the relation between α, $d\alpha/dt$ and t are discussed quantitatively.

4. A trial of quantitative analysis

When a material decomposes with several consecutive reactions, simulation will be a useful tool to analyze the decomposition behavior. The reaction model used for simulation is as follows: The starting material A decomposes into R_1 and P_1 by the first reaction (reaction 1), and P_1 vaporizes. By the second reaction (reaction 2), R_1 decomposes into R_2 and P_2, and P_2 vaporizes. By the third reaction (reaction 3), R_2 vaporizes. To distinguish vaporized R_2 from residual R_2, vaporized R_2 is written as P_3.

The reactions above described and mass fraction of related materials are expressed as follows:

$$\text{Reaction 1}: \quad \overset{X_1}{\mathrm{A}} \rightarrow \overset{C_1}{\mathrm{R_1}} + \overset{C_1}{\mathrm{P_1}} \uparrow$$

$$\text{Reaction 2}: \quad \overset{X_2}{\mathrm{R_1}} \rightarrow \overset{C_2}{\mathrm{R_2}} + \overset{C_2}{\mathrm{P_2}} \uparrow$$

$$\text{Reaction 3}: \quad \overset{X_3}{\mathrm{R_2}} \rightarrow \overset{C_3}{\mathrm{P_3}} \uparrow$$

where X_1, X_2 and X_3 are the mass fractions of the residual A, R_1 and R_2, and, C_1, C_2 and C_3 are the conversions of P_1, P_2 and P_3 at t, respectively. If the following reactions do not occur, the conversions of R_1 and R_2 are equal to C_1 and C_2, respectively.

The rate equation is usually expressed with mole fractions. TG gives only the information of total mass and the rate of total mass loss. Therefore, it is necessary to convert mole fractions of components in rate equations to mass fractions, and to describe total fraction of mass loss with mass fractions of components.

Considering the material balance of above reactions, the relationships between mass fractions are expressed by the following equations (see Appendix A):

$$\alpha = a_1C_1 + a_2C_2 + a_3C_3 \tag{1}$$

$$X_1 + C_1 = 1, \quad X_2 + C_2 = C_1, \quad X_3 + C_3 = C_2 \tag{2}$$

$$X = X_1 + (a_2 + a_3)X_2 + a_3X_3 = 1 - \alpha \tag{3}$$

where a_1, a_2 and a_3 are the fraction of total mass loss for each reaction.

Only when coexisting materials do not influence the reactions, the rate equations are described with mass fractions. If coexisting materials influence the reactions, the rate equations are described with mole fractions. To analyze the results of thermogravimetry kinetically, it is necessary to describe mole fractions with mass fractions. The relationships between the mass fractions and the mole fractions of A, R_1 and R_2 are expressed by following equations (see Appendix A):

$$n_A = \frac{X_1}{X_1 + N_1X_2 + N_3X_3} \tag{4}$$

$$n_{R_1} = \frac{N_1X_2}{X_1 + N_1X_2 + N_3X_3} \tag{5}$$

$$n_{R_2} = \frac{N_3X_3}{X_1 + N_1X_2 + N_3X_3} \tag{6}$$

where n_A, n_{R_1} and n_{R_2} are the mole fractions of A, R_1 and R_2, respectively. As the materials in the sample do not influence the vaporized materials, the mole fractions of vaporized materials are equal to mass fractions. Namely, the mole fractions of P_1, P_2 and P_3 vaporized till t, n_{P_1}, n_{P_2} and n_{P_3} are equal to C_1, C_2 and C_3, respectively (see Appendix A).

As described before, reaction (1) is considered to be the first- or the second-order reaction. If reaction (1) is the second-order reaction, or, if it is influenced by coexisting materials, the rate of reaction (1) becomes too slow, and reaction (1) does not end within the time that the decomposition reaction was observed. Therefore, it is concluded that reaction (1) is the first-order reaction and is not influenced by the presence of the coexisting materials. The rate equation of reaction (1) is given by

$$-\frac{\mathrm{d}X_1}{\mathrm{d}t} = k_1X_1$$

As $X_1=1-C_1$, we obtain

$$C_1 = 1 - \exp(-k_1t),$$
$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = k_1(1-C_1) = k_1\exp(-k_1t) \qquad (7)$$

As $C_1 \approx \alpha/a_1$ when C_2 and C_3 are small, $\mathrm{d}\alpha/\mathrm{d}t \approx k_1(a_1-\alpha)$ is obtained. From Fig. 5, the mean value of a_1 is 0.39. k_1 is the slope of linear parts of the plot of $\mathrm{d}\alpha/\mathrm{d}t$ against α in Fig. 4.

Reaction (2) is considered to be chain reaction or the random scission of main chain of polymer. If reaction (2) is random scission of main chain, the value of α at the peak of $\mathrm{d}\alpha/\mathrm{d}t$ becomes smaller than the observed value though the result is not shown. Therefore, it is concluded that reaction (2) is chain reaction. The simplest chain reaction is written as follows:

$$\overset{X_2}{\mathrm{R}_1} \rightarrow \overset{X_3}{\mathrm{R}_2} + \overset{C_2}{\mathrm{P}_2} \uparrow$$
$$\overset{X_2}{\mathrm{R}_1} + \overset{X_3}{\mathrm{R}_2} \rightarrow \overset{X_3}{\mathrm{R}_2} + \beta\overset{C_2}{\mathrm{P}_2} \uparrow$$

If coexisting materials do not influence the rate of reaction, the rate of each reaction is expressed by

$$\frac{\mathrm{d}C_2}{\mathrm{d}t} = k_2''X_2$$
$$\frac{\mathrm{d}C_2}{\mathrm{d}t} = \beta k_2'X_2X_3 - k_2'X_2X_3$$

Total rate of reaction (2) is expressed by

$$\frac{\mathrm{d}C_2}{\mathrm{d}t} = k_2X_2(X_3+f)$$

where $f = k_2''/k_2'(\beta-1)$ and $k_2 = k_2'(\beta-1)$. If coexisting materials influence the rate of reaction (2), the rate equation is expressed by

$$\frac{\mathrm{d}C_2}{\mathrm{d}t} = k_2n_{\mathrm{R}_1}(n_{\mathrm{R}_2}+f) \qquad (8)$$

Numerical integration of $\mathrm{d}C_2/\mathrm{d}t$ gives C_2.

Reaction (3) is supposed to be vaporization of residual materials. If the vaporization rate is proportional to vapor pressure and the vapor pressure is proportional to the mole fraction of R_2 in residue, the rate of vaporization is expressed by

$$\frac{\mathrm{d}C_3}{\mathrm{d}t} = k_3n_{\mathrm{R}_2} \qquad (9)$$

Numerical integration of $\mathrm{d}C_3/\mathrm{d}t$ gives C_3.

α and $\mathrm{d}\alpha/\mathrm{d}t$ is given by

$$\alpha = a_1C_1 + a_2C_2 + a_3C_3$$
$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = a_1\frac{\mathrm{d}C_1}{\mathrm{d}t} + a_2\frac{\mathrm{d}C_2}{\mathrm{d}t} + a_3\frac{\mathrm{d}C_3}{\mathrm{d}t}$$

The calculated results of α, $\mathrm{d}\alpha/\mathrm{d}t$ and t are compared with the experimental results. The values of a_2, a_3, k_1, k_2, k_3, f, N_1 and N_3 are determined as the values of these parameters when the experimental results are well reproduced by the calculated results.

The temperature dependence of k_i (i=1, 2 or 3) is expressed by Arrhenius equation

$$k_i = A_i\exp - \frac{E_i}{RT}$$

From the values of slopes of linear parts in Fig. 4, E_1 is roughly estimated as 197 kJ mol^{-1}. If temperature dependence of k_2 and k_2'' is different, f also depends on temperature. The mean value of E_2 and E_3 will be 206 kJ mol^{-1}.

Using the model described above, the decomposition behaviors of the fluororubber are simulated. The value of a_1 used in the simulation is fixed at 0.39. When a_2 is 0.15, a_3 is 0.46, and, N_1 and N_3 are 2, the experimental results are well reproduced with this model. Fig. 6 shows the calculated and the observed relations between α and t. Difference between the observed and the calculated results shown in Fig. 6 is within experimental error.

Fig. 7 shows the calculated and the observed relationships between $\mathrm{d}\alpha/\mathrm{d}t$ and α. Considering that the noise level of $\mathrm{d}\alpha/\mathrm{d}t$ is ±0.0002 to ±0.0003 min^{-1}, the observed data is almost reproduced by the calculated curves though the deviation seems slightly larger than this noise level. Fig. 8 shows the observed data of $\mathrm{d}\alpha/\mathrm{d}t$ against α at 400.7°C and the calculated curves of $a_1\mathrm{d}C_1/\mathrm{d}t$, $a_2\mathrm{d}C_2/\mathrm{d}t$, $a_3\mathrm{d}C_3/\mathrm{d}t$ and $\alpha/\mathrm{d}t$ against α. The shapes of the curves of $a_1\mathrm{d}C_1/\mathrm{d}t$ and $a_2\mathrm{d}C_2/\mathrm{d}t+a_3\mathrm{d}C_3/\mathrm{d}t$ against α are similar to the curve of types A and B in Fig. 6, respectively.

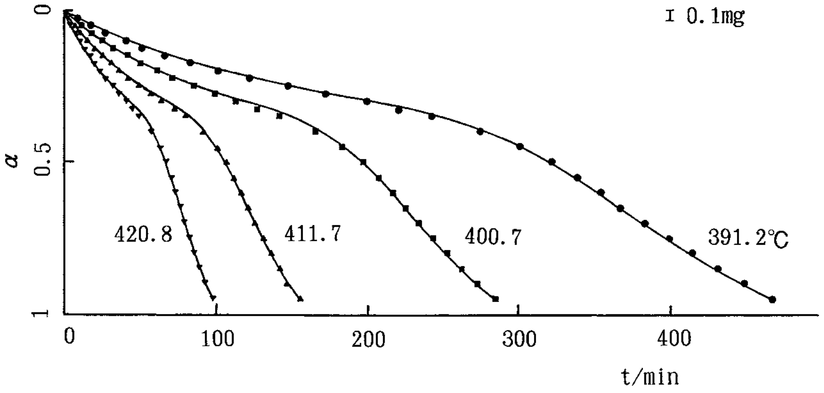

Fig. 6. Plots of the observed and the calculated relations between α and t. Solid lines show the calculated results.

Fig. 9 shows Arrhenius plots of k_1, k_2 and k_3. The values of activation energies and pre-exponential factors are shown in Table 1. The differences between E_1, E_2 and E_3 are small. This is the reason that the consecutive reactions are observed. E_2 is slightly larger than E_1 and E_3, as it is pointed out from the results shown in Fig. 1. The value of E_1 is almost equal to the estimated value, 197 kJ mol^{-1}. The mean value of E_2 and E_3 is 206.5 kJ mol^{-1} and is equal to 206 kJ mol^{-1}, which is obtained by the superposition shown in Fig. 3. The values of f depend on temperature slightly.

The shape of the curve of type C in Fig. 5 could not be reproduced by the model above described and the values of parameters used. This means that the model or the values of parameters used are not yet sufficient. Considering the noise level of dα/dt, there is a possibility that the value of a_1 is overestimated. As described before, it is possible that the number of reactions is not three but four. Further, if, for example, A is insoluble in R_1 and R_2, X_1 in Eqs. (5) and (6) should be eliminated. However, as the relations between α and t are well reproduced and the difference

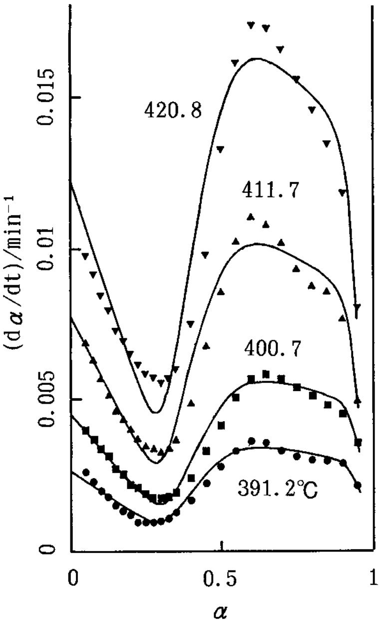

Fig. 7. Plots of the observed and the calculated relations between dα/dt and α. Solid lines show the calculated results.

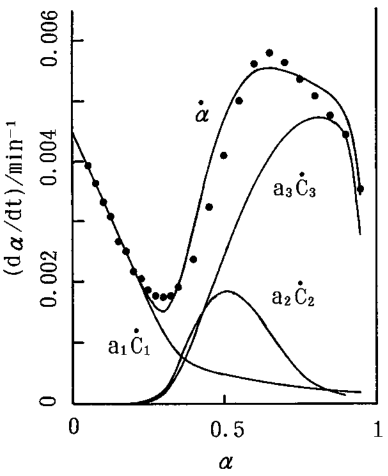

Fig. 8. Curves of the calculated dα/dt, a_1dC_1/dt, a_2dC_2/dt, a_3dC_3/dt, and, the observed dα/dt against α at 400.7°C.

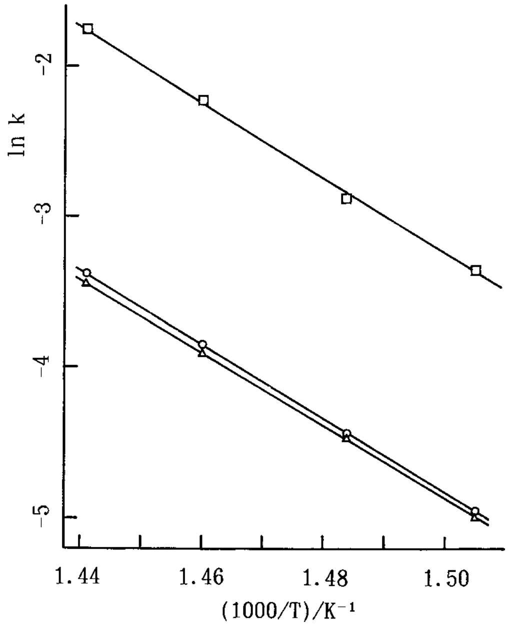

Fig. 9. Arrhenius plots of k_1 (△), k_2 (○) and k_3 (□).

Table 1
Activation energies and pre-exponential factors[a]

Reaction constants	A (min^{-1})	E (kJ mol^{-1})
k_1	3.32×10^{13}	199
k_2	1.05×10^{15}	210
k_3	6.88×10^{13}	203
k_2''	7.48×10^{9}	188

[a] $k_2''=fk_2$.

between the observed and the calculated values of dα/dt are only slightly larger than noise level, these possibilities are not examined in this paper. For further detailed discussion, the improvement of precision of dα/dt is necessary.

Appendix A.

The symbols of the materials are used as the suffixes of symbols of mass, w, number of molecules, N, molecular weight, M, and mole fractions, n, in order to express the values of the materials. When reactions (1)–(3) are assumed, the material balance of A, R_1, P_1, R_2, P_2 and P_3 is expressed by following equations:

$$w_A(0) = w_A(t) + w_{R_1B}(t) + w_{P_1}(t)$$

$$w_A(0) = w_{R_1B} + w_{P_1}$$

$$w_{R_1B}(t) = w_{R_1}(t) + w_{P_2}(t) + w_{R_2B}(t)$$

$$w_{R_1B} = w_{R_2B} + w_{P_2} = w_{P_2} + w_{P_3}$$

$$w_{R_2B}(t) = w_{R_2}(t) + w_{P_2}(t)$$

$$w_{R_2B} = w_{P_3}$$

$$w_P(t) = w_{P_1}(t) + w_{P_2}(t) + w_{P_3}(t)$$

$$w(t) = w_A(t) + w_{R_2}(t) + w_{R_3}(t)$$

where 0 and t in the parentheses show the time. The symbols without brackets are the values of final state. Suffixes R_1B and R_2B show the hypothetical values if the following reactions do not occur. $w_{R_1B}(t)$ is proportional to $w_{P_1}(t)$ and $w_{R_2B}(t)$ is proportional to $w_{P_2}(t)$. $w_P(t)$ is the total mass loss and $w(t)$ is the total residual mass at time t.

C_1, C_2 and C_3 are defined by

$$C_1 = \frac{w_{P_1}(t)}{w_{P_1}} = \frac{w_{R_1B}(t)}{w_{R_1B}}$$

$$C_2 = \frac{w_{P_2}(t)}{w_{P_2}} = \frac{w_{R_2B}(t)}{w_{R_2B}}$$

$$C_3 = \frac{w_{P_3}(t)}{w_{P_3}}$$

In the real decomposition reactions, the quantity of R_1 and R_2 decreases by the following reactions. X_1, X_2 and X_3 at t are defined by

$$X_1 = \frac{w_A(t)}{w_A(0)}$$

$$X_2 = \frac{w_{R_1}(t)}{w_{R_1B}}$$

$$X_3 = \frac{w_{R_2}(t)}{w_{R_2B}}$$

The fractions of total mass loss for each reaction, a_1, a_2 and a_3 are defined by

$$a_1 = \frac{w_{P_1}}{w_A(0)}$$

$$a_2 = \frac{w_{P_2}}{w_A(0)}$$

$$a_3 = \frac{w_{\mathrm{P}_3}}{w_\mathrm{A}(0)}$$

Fraction of total residual mass, X, and that of total mass loss, α, are defined by

$$X = \frac{w(t)}{w_\mathrm{A}(0)}$$

$$\alpha = \frac{w_\mathrm{P}(t)}{w_\mathrm{A}(0)}$$

From these equations, the following relationships are obtained:

$$\alpha = a_1C_1 + a_2C_2 + a_3C_3 \tag{A.1}$$

$$X_1 + C_1 = 1, \quad X_2 + C_2 = C_1, \quad X_3 + C_3 = C_2 \tag{A.2}$$

$$X = X_1 + (a_2 + a_3)X_2 + a_3X_3 = 1 - \alpha \tag{A.3}$$

If coexisting materials do not influence the reactions, the rate equations are described using these equations. If coexisting materials influence the reactions, it is necessary to describe mole fractions with mass fractions. Using molecular weight, M, and number of molecules, N, mole fraction is converted to mass fraction. The starting material A is crosslinked polymer. However, from the point of view of decomposition reactions, it is assumed that A has a hypothetical molecular weight, M_A, and the sample is composed of a hypothetical number of molecules, N_A. From N_A molecules of A, N_{P_1} molecules of P_1 and N_{R_1} molecules of R_1 are produced by reaction (1). N_{R_1} is a hypothetical value when the second reaction does not occur. $N_{\mathrm{R}_1}/N_\mathrm{A}=N_1$ is the number of molecules of R_1 produced from 1 mol of A.

For reaction (2), it is assumed that one molecule of R_1 produces N_{P_2} molecules of P_2 and N_{R_2} molecules of R_2. When reaction (3) does not occur, $N_{\mathrm{R}_1}N_{\mathrm{R}_2}$ molecules of R_2 and $N_{\mathrm{R}_2}N_{\mathrm{P}_2}$ molecules of P_2 are produced from N_A molecules of A. If the number and the molecular weight of R_2 does not change by reaction (3), then N_{R_2} is equal to N_{P_3} and M_{R_2} is equal to M_{P_3}. The number of molecules of P_3 produced from N_A molecules of A is $N_{\mathrm{R}_1}N_{\mathrm{P}_3} = N_{\mathrm{R}_1}N_{\mathrm{R}_2}$. $N_{\mathrm{R}_1}N_{\mathrm{P}_3}/N_\mathrm{A} = N_3$ is the number of moles of R_2 and P_3 produced from 1 mol of A.

The numbers of residual molecules of A, R_1 and R_2 at t are denoted by $N_\mathrm{A}(t)$, $N_{\mathrm{R}_1}(t)$ and $N_{\mathrm{R}_2}(t)$, respectively. These are related to mass fraction as follows:

$$N_\mathrm{A}(t) = N_\mathrm{A}\frac{M_\mathrm{A}N_\mathrm{A}(t)}{M_\mathrm{A}N_\mathrm{A}} = N_\mathrm{A}X_1$$

$$N_{\mathrm{R}_1}(t) = N_{\mathrm{R}_1}\frac{M_{\mathrm{R}_1}N_{\mathrm{R}_1}(t)}{M_{\mathrm{R}_1}N_{\mathrm{R}_1}} = N_{\mathrm{R}_1}X_2$$

$$N_{\mathrm{R}_2}(t) = N_{\mathrm{R}_1}N_{\mathrm{R}_2}\frac{M_{\mathrm{R}_2}N_{\mathrm{R}_2}(t)}{M_{\mathrm{R}_2}N_{\mathrm{R}_1}N_{\mathrm{R}_2}} = N_{\mathrm{R}_1}N_{\mathrm{R}_2}X_3$$

The number of vaporized molecules till t, $N_{\mathrm{P}_1}(t)$, $N_{\mathrm{P}_2}(t)$ and $N_{\mathrm{P}_3}(t)$, respectively, are related to mass fraction as follows:

$$N_{\mathrm{P}_1}(t) = N_{\mathrm{P}_1}\frac{M_{\mathrm{P}_1}N_{\mathrm{P}_1}(t)}{M_{\mathrm{P}_1}N_{\mathrm{P}_1}} = N_{\mathrm{P}_1}C_1$$

$$N_{\mathrm{P}_2}(t) = N_{\mathrm{R}_1}N_{\mathrm{P}_2}\frac{M_{\mathrm{P}_2}N_{\mathrm{P}_2}(t)}{M_{\mathrm{P}_2}N_{\mathrm{R}_1}N_{\mathrm{P}_2}} = N_{\mathrm{R}_1}N_{\mathrm{P}_2}C_2$$

$$N_{\mathrm{P}_3}(t) = N_{\mathrm{R}_1}N_{\mathrm{P}_3}\frac{M_{\mathrm{P}_3}N_{\mathrm{P}_3}(t)}{M_{\mathrm{P}_3}N_{\mathrm{R}_1}N_{\mathrm{P}_3}} = N_{\mathrm{R}_1}N_{\mathrm{P}_3}C_3$$

Mole fractions of residual A, R_1 and R_2 at t are denoted by n_A, n_{R_1} and n_{R_2}, respectively. These are expressed by mass fractions as follows:

$$n_\mathrm{A} = \frac{N_\mathrm{A}(t)}{N_\mathrm{A}(t) + N_{\mathrm{R}_1}(t) + N_{\mathrm{R}_2}(t)} = \frac{X_1}{X_1 + N_1X_2 + N_3X_3} \tag{A.4}$$

$$n_{\mathrm{R}_1} = \frac{N_{\mathrm{R}_1}(t)}{N_\mathrm{A}(t) + N_{\mathrm{R}_1}(t) + N_{\mathrm{R}_2}(t)} = \frac{N_1X_2}{X_1 + N_1X_2 + N_3X_3} \tag{A.5}$$

$$n_{\mathrm{R}_2} = \frac{N_{\mathrm{R}_2}(t)}{N_\mathrm{A}(t) + N_{\mathrm{R}_1}(t) + N_{\mathrm{R}_2}(t)} = \frac{N_3X_3}{X_1 + N_1X_2 + N_3X_3} \tag{A.6}$$

Mole fractions of P_1, P_2 and P_3 vaporized till t are denoted by n_{P_1}, n_{P_2} and n_{P_3}, respectively. These are expressed by mass fractions as follows:

$$n_{\mathrm{P}_1} = \frac{N_{\mathrm{P}_1}(t)}{N_{\mathrm{P}_1}} = C_1 \tag{A.7}$$

$$n_{\mathrm{P}_2} = \frac{N_{\mathrm{P}_2}(t)}{N_{\mathrm{R}_1}N_{\mathrm{P}_2}} = C_1 \tag{A.8}$$

$$n_{\mathrm{P}_3} = \frac{N_{\mathrm{P}_3}(t)}{N_{\mathrm{R}_1}N_{\mathrm{P}_3}} = C_3 \tag{A.9}$$

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